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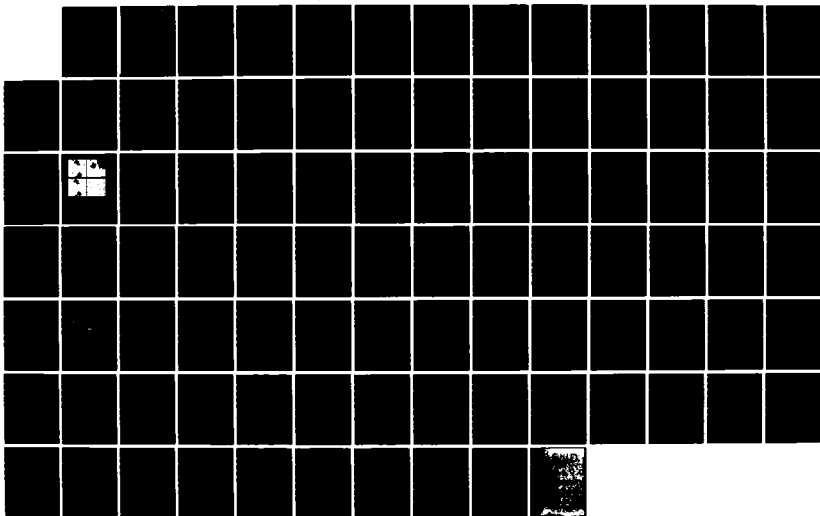
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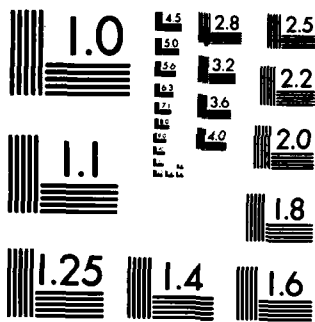
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VOLUME 2. A PROPOSAL FOR A POLYMER RESEARCH CENTER
AT THE ATLANTA UNIVERSITY

Volume 1. Malcolm B. Polk, Kofi B. Bota

Volume 2. Malcolm B. Polk, Kofi B. Bota, Harold Banks,
Yitbarek H. Mariam, and James L. Reed
Department of Chemistry
Atlanta University
Atlanta, Georgia 30314

Under

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Office of Naval Research
Arlington, Virginia 22217

OFFICE OF NAVAL RESEARCH
Resident Representative
Georgia Institute of Technology
206 O'Keefe Building
Atlanta, Georgia 30332

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Report NR 631-745

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A number of block copolyesters containing benzene and cyclohexane rings have been synthesized and shown to form liquid crystalline solutions. The block copolyesters have been characterized by NMR, IR, DSC, TGA and polarizing optical microscopy analysis. | | |

20.

A Polymer Research Center has been developed to (1) conduct research, (2) train and educate students at the M.S. and Ph.D. level, (3) conduct or sponsor short courses, (4) serve as host during summers or sabbaticals to professors, and (5) pursue cooperative arrangements with local universities.

As part of the research mission of the Polymer Research Center, all-aromatic block copolyesters have been synthesized and characterized. Some of these block copolyesters contain the o,o'-diphenylene ring system. Bicyclo[2.2.2]octane-1,4-dicarboxylic acid and bicyclo[2.2.2]octane-1,4-diol have been synthesized and bicyclo[2.2.2]octane-1,4-dicarboxylic acid has been incorporated into several polymers. Active moiety containing polymers of the (polystyrene) \rightarrow CH₂-(tet-b) and (polystyrene) \rightarrow CH₂-(tet-b)CoCl₃ type have been prepared and characterized. Several potentially "Comb-Like" liquid crystalline polymers have been synthesized for conversion into "Comb-Like" liquid crystalline ion-containing polymers.

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VOLUME 1. SYNTHESIS AND CHARACTERIZATION OF UNIQUE LIQUID CRYSTALLINE
BLOCK COPOLYESTERS

INTRODUCTION

Nature and Scope of the Problem

A number of research teams have prepared liquid crystalline polyesters.¹⁻¹⁹ These thermotropic polyesters are generally insoluble in ordinary solvents and in the melt, these liquid crystals may be oriented under shear at the spinneret and coagulation of the fiber sets the orientation and results in fibers having unusually high strength and modulus.

The fibers spun from rod-like thermotropic polymers generally have high melting points. Although a high melting temperature is important for many end-use applications, when it exceeds the decomposition temperature of the resin, it becomes a liability. Polymers incorporating unsymmetrical monomers and/or random copolymer units have been prepared in order to decrease their melting points to below the decomposition point of rod-like polyesters having high symmetry.

The objectives of the Polk and Bota research team were to prepare liquid crystal block copolyesters which contain cyclohexane and benzene rings. The properties of block copolymers resemble those of incompatible physical blends in some respects and homogenous random copolymers in other respects. Due to the presence of the intersegment bond which prevents the segments from separating, block copolymers usually exhibit two-phase ^{morphology} ~~morphology~~ which on the micro level is similar to that of polymer blends on the macro-level. Instead of the averaging of the properties of the different components as found in homogenous

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random copolymers, block copolymers display the properties characteristic of each of the components plus some new properties due to the block copolymer morphology. The objectives of the Polk and Bota research team were to use cyclohexane derivatives as the soft blocks and benzene derivatives as the hard blocks and to optimize the solubility, thermal, and mechanical properties of the resulting $(A-B)_n$ block copolyesters while increasing the thermoplastic elastomeric character.

MAIN TEXT

Liquid Crystalline Polyesters Synthesized

Poly(cis, trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-1,4-phenylene terephthalate)I, poly(cis, trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate)II, poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-1,4-phenylene terephthalate)VII, poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-methylphenylene terephthalate)IX, and poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate)X have been synthesized and shown to form lyotropic solutions. However only poly(cis,trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate)II had a melting point low enough conceivably for melt spinning although it melted with decomposition.

Other Polyesters Synthesized

Also poly(trans-1,2-cyclohexylene-trans-1,2-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) V, poly(trans-1,2-cyclohexylene-trans-1,2-cyclohexanedioate-b-2-methyl-1,3-phenylene isophthalate)IV, poly(cis,trans-1,2-cyclohexylene-cis,trans-1,2-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) (III and V), and poly(cis,trans-1,2-cyclohexylene-cis,trans-1,2-cyclohexanedioate-b-1,4-phenylene isophthalate) (IV and VI) have been synthesized. Only poly(trans-1,2-cyclohexylene-trans-1,2-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate)V had a high enough molecular weight and low enough melting point for melt spinning. The fibers obtained, however, were amorphous. The structure of a number of the block copolyesters synthesized are shown in Figure 1. All attempts to synthesize cis polymers like III, IV, and VIII led to the isolation of the corresponding (cis,trans) cyclohexylene moieties along

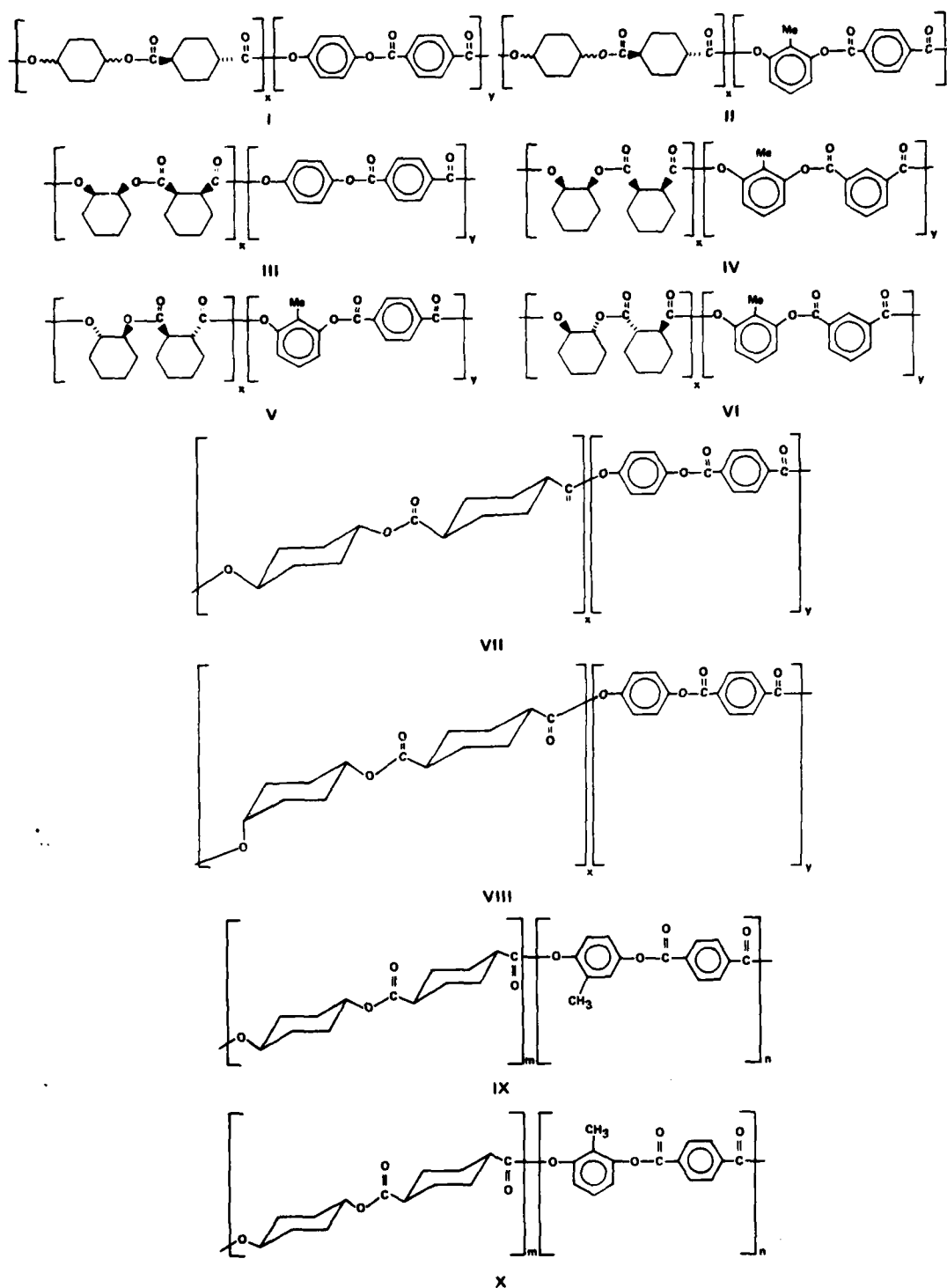


Figure 1. Structures of Block Copolyesters

the polymer chain.

Synthetic Procedures and Properties of the Polyesters

All but one of the block copolyesters were formed by the step-reaction condensation of cycloaliphatic ester oligomers capped with dihydroxy end groups and aromatic ester oligomers capped with dicarboxylic acid chloride end groups (Figure 2). Poly(cis,trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) was prepared by the condensation of cycloaliphatic ester and aromatic ester oligomers end-capped with hydroxyl groups with terephthaloyl chloride (Figure 3). The oligomers were formed by using a 10 mole % excess of acid chloride in one case and a 10 mole % excess of dihydroxy compound in the other. Some synthetic procedures are presented in detail below.

Inherent viscosities were measured at 30°C in m-cresol and o-chlorophenol at a concentration of 0.50g/100 mL except in those cases specified. Melting points and glass transition temperatures were determined with a differential scanning calorimeter (DuPont 990 and 1090 thermal analyzers with the DuPont 910 differential scanning calorimeter). NMR spectra were determined in chloroform solutions of polyesters with a Bruker WH-250 spectrometer with proton spectra taken at 250.133 MHz and carbon-13 spectra at 62.860 MHz. Infrared spectra were obtained on KBr disks with a Beckman 4240 infrared spectrophotometer. Polarizing microscopy was performed on an Aus Jena Amplival Pol. D polarizing microscope. Elemental analysis data were provided by Galbraith Laboratories.

A. Preparation of Poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl] (I).

A 250-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap

SYNTHESIS OF BLOCK COPOLYESTERS

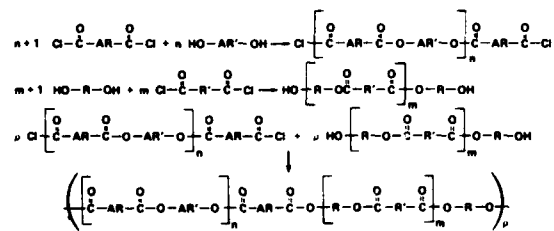


Figure 2. Synthetic Scheme for Block Copolyesters

Synthesis of Block Copolyester

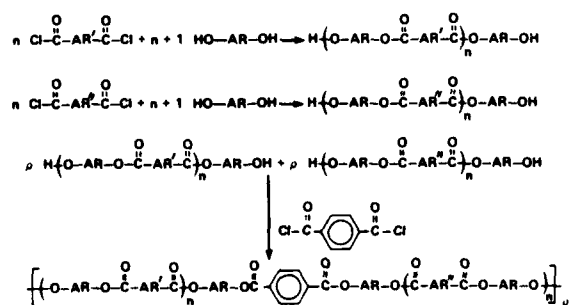


Figure 3. Alternative Synthetic Scheme for Block Copolyesters

was charged with 4.18g (0.0200 mol) of trans-1,4-cyclohexanedicarbonyl chloride, 2.56g (0.0220 mol) of 1,4-cyclohexanediol and 40 mL of dry *o*-dichlorobenzene. The reactor was purged continuously with nitrogen. The mixture was heated at 85-110°C for 45 min, during which time the evolution of HCl was vigorous. The mixture was refluxed for 2.5 h.

A 250-mL three-necked, round bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap was charged with 4.40g (0.0400 mol) of hydroquinone, 8.93g (0.0440 mol) of terephthaloyl chloride, and 40 mL of dry *o*-dichlorobenzene. The reactor was purged continuously with nitrogen. The mixture was heated for 45 min at 85-110°C, accompanied by the evolution of HCl. The mixture was refluxed for 2.5 h.

After the two different polymer solutions had been allowed to cool, 20 mL of each of the solutions were thoroughly mixed and refluxed for 1 h under an atmosphere of nitrogen. The block copolyester, poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenylene-oxyterephthaloyl], was collected and washed with water and acetone. The block copolyester was dried at 220°C for 24 h in a vacuum oven.

Elemental analysis showed a number average degree of polymerization of 8 for the poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] oligomer. Anal. Calcd for $H(C_{14}H_{20}O_4)_8C_6H_{11}O_2 \cdot 2H_2O$: C, 65.31; H, 8.11. Found: C, 65.30; H, 7.82. Elemental analysis showed a number average degree of polymerization of 12 for the poly(oxy-1,4-phenylene-oxyterephthaloyl) oligomer. Anal. Calcd. for $HO(C_{14}H_8O_4)_{12}C_8H_5O_3 \cdot 2H_2O$: C, 68.53; H, 3.44. Found: C, 68.52; H, 3.67. The inherent viscosity of the block copolyester was 0.39 dL/g in *o*-chlorophenol at 30°C.

The infrared spectrum showed peaks at 3420 (-OH stretch), 2940 and 2860 (aliphatic C-H stretch), 1720 (ester C=O stretch), 1600 and 1500 (aromatic

nucleus) and 1250, 1080, 1040, and 1010 (C-O stretch) cm^{-1} .

The differential scanning calorimetry thermogram of poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] showed a crystalline melting point at 238°C. The differential scanning calorimetry thermogram of the corresponding block copolyester showed a crystalline melting peak at 242°C. The other melting peak was obscured by decomposition.

B. Preparation of Poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II).

The same procedure described in A was followed. For the preparation of the cycloaliphatic oligomer, 4.71g (0.0220 mol) of trans-1,4-cyclohexanedicarbonyl chloride, 2.87g (0.0247 mol) of 1,4-cyclohexanediol, and 20 mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 5.48g (0.0440 mol) of 2-methylresorcinol, 8.14g (0.0400 mol) of terephthaloyl chloride, and 40 mL of dry o-dichlorobenzene were used. Terephthaloyl chloride (0.6348g), was added to a refluxing mixture of 10 mL each of the two oligomer solutions to form the block copolyester. The mixture was refluxed for another 30 min.

Elemental analysis showed a number average degree of polymerization of 18 for the poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] oligomer. Anal. Calcd for $\text{H}(\text{C}_{14}\text{H}_{20}\text{O}_4)_{18}\text{C}_6\text{H}_{11}\text{O}_2$: C, 66.55; H, 8.00. Found: C, 66.53; H, 8.03. Elemental analysis showed a number average degree of polymerization of 18 for the poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl]oligomer. Anal. Calcd for $\text{H}(\text{C}_{15}\text{H}_{10}\text{O}_4)_{18}\text{C}_7\text{H}_7\text{O}_2$: C, 70.78; H, 4.00. Found: C, 69.68; H, 3.95. The inherent viscosities of poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were 0.38 and 0.49 dL/g, respectively at 30°C in o-chlorophenol. The inherent viscosity of the corresponding block

copolyester was 0.54 dL/g at 30°C in o-chlorophenol.

The infrared spectrum showed peaks at 3490 (-OH stretch), 3060 (aromatic C-H), 2930 and 2860 (aliphatic C-H), 1720 (ester C=O stretch), 1605, 1575, and 1460 (aromatic C=C in-plane vibrations), and 1245, 1080, and 1035 (C-O stretch) cm^{-1} .

The differential scanning calorimetry thermogram of poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] showed a crystalline melting point of 225°C. The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] showed a crystalline melting peak at 313°C. The differential scanning calorimetry thermogram of the corresponding block copolyester showed a crystalline melting peak at 220°C. The other melting peak was obscured by decomposition.

The ^{13}C NMR spectrum of the block copolymer was obtained in CDCl_3 . The ^{13}C chemical shifts and integrals were as follows: δ 27.4 (10.6), 27.7 (19.3), 28.1 (38.5), 29.0 (0.4), 29.2 (0.7), 42.8 (13.8), 69.8 (5.1), 70.6 (9.4), 120.2 (1.7), 127.0 (1.0), 130.6 (8.4), 150.3 (1.6), 163.8 (1.0), 174.9 (3.0), and 175.0 (6.0). The low-field peaks (δ 175.0, 174.9, and 163.8) correspond to carbonyl carbons. The resonances at δ 120.2-150.3 represent aromatic carbons, and the resonances at δ 27.4-70.6 represent aliphatic carbons.

Tetrachloroethane-o-chlorophenol-phenol and o-chlorophenol solutions of the block copolyester depolarized plane-polarized light when thin layers of the solutions were viewed at 158 X magnification at 24°C. For the 60:30:10 v/v/v tetrachloroethane:o-chlorophenol:phenol solutions, a 15% by weight solution of the block copolyester was strongly anisotropic and a 10% by weight solution of the block copolyester was only weakly anisotropic.

C. Preparation of Poly[oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] (VI).

The same procedure in A was followed except that the o-dichlorobenzene was removed by vacuum distillation at 86°C/14mm. For the preparation of the cycloaliphatic oligomer, 15.4g(0.0736 mol) of trans-1,2-cyclohexanedicarbonyl chloride, 9.40g (0.0892 mol) of trans-1,2-cyclohexanediol, and 55 mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 13.8g (0.0683 mol) of isophthaloyl chloride, 7.71g (0.0621 mol) of 2-methylresorcinol, and 45 mL of dry o-dichlorobenzene were used.

Elemental analysis showed a number average degree of polymerization of 7 for the poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H(C_{14}H_{20}O_4)_7C_6H_{11}O_2$: C, 65.13; H, 8.14. Found: C, 65.11; H, 7.95. Elemental analysis showed a number average degree of polymerization of 5 for the poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] oligomer. Anal. Calcd for $HO(C_{15}H_{10}O_4)_5C_8H_5O_3$: C, 69.36; H, 3.89. Found: C, 69.31; H, 3.83. The inherent viscosities of poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] were 0.16 and 0.20 dL/g, respectively, at 30°C in m-cresol. The inherent viscosity of the corresponding block copolyester was 0.26 dL/g at 30°C in m-cresol.

The infrared spectrum showed peaks at 3420 (-OH stretch), 2965 and 2850 (aliphatic C-H stretch), 1730 (ester C=O stretch), 1600 and 1460 (aromatic nucleus), and 1290, 1080, 1035, and 1000 (C-O stretch) cm^{-1} .

The differential scanning calorimetry thermogram of poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) showed a glass transition temperature of 68°C. The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] showed a glass transi-

tion temperature of 75°C. The differential scanning calorimetry thermogram of the corresponding block copolyester showed a glass transition temperature of 90°C and a crystalline melting point of 195°C.

The ^{13}C NMR spectrum of the block copolymer was obtained in CDCl_3 . The ^{13}C chemical shifts and integrals were as follows: δ 10.2 (20.3), 21.3 (4.3), 22.0 (5.7), 23.2 (23.6), 23.7 (21.1), 25.2 (15.8), 26.1 (7.5), 28.8 (23.5), 29.9 (19.3), 40.5 (7.4), 42.3 (12.9), 42.4 (13.6), 42.5 (11.0), 42.7 (11.3), 44.6 (9.2), 73.2 (6.4), 120.1 (16.7), 123.9 (6.8), 126.9 (9.7), 129.5 (10.2), 130.1 (13.7), 131.9 (10.2), 135.2 (17.0), 150.2 (13.9), 163.7 (11.6), 174.2 (18.2), and 174.5 (6.5). The low-field peaks (δ 174.5, 174.2, and 163.7) correspond to carbonyl carbons. The resonances at δ 120.1–150.2 represent aromatic carbons, and the resonances at δ 10.2–73.2 represent aliphatic carbons.

D. Preparation of Poly[oxy-cis,trans-1,2-cyclohexyleneoxycarbonyl-cis,trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] (IV and VI).

The same procedure in A was followed except the o-dichlorobenzene was removed by vacuum distillation at 86°C/14 mm. For the preparation of the cycloaliphatic oligomer, 12.1g (0.0577 mol) of cis-hexahydrophthalic acid chloride, 7.38g (0.0635 mol) of cis-1,2-cyclohexanediol, and 43 mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 13.8g (0.0683 mol) of isophthaloyl chloride, 7.70g (0.0621 mol) of 2-methylresorcinol, and 50 mL of dry o-dichlorobenzene were used.

Elemental analysis showed a number average degree of polymerization of 3 for the poly(oxy-cis,trans-1,2-cyclohexyleneoxycarbonyl-cis,trans-1,2-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $\text{H}(\text{C}_{14}\text{H}_{20}\text{O}_4)_3\text{C}_6\text{H}_{11}\text{O}_2$: C, 62.88; H, 7.64. Found: C, 62.28; H, 7.63. Elemental analysis showed a number average

degree of polymerization of 3 for the poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] oligomer. Anal. Calcd for $\text{HO}(\text{C}_{15}\text{H}_{10}\text{O}_4)_3\text{C}_8\text{H}_5\text{O}_3$: C, 68.53; H, 3.88. Found: C, 68.41; H, 4.07. The inherent viscosities of poly(oxy-cis,trans-1,2-cyclohexyleneoxycarbonyl-cis,trans-1,2-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] were 0.06 and 0.21 dL/g, respectively, at 30°C in m-cresol. The inherent viscosity of the corresponding block copolyester was 0.25 dL/g at 30°C in m-cresol.

The infrared spectrum showed peaks at 3400 (-OH stretch), 2920 and 2850 (aliphatic C-H stretch), 1720 (ester C=O stretch), 1600, 1575, and 1440 (aromatic C=C in-plane vibrations), and 1280, 1160 and 1030 (C-O stretch) cm^{-1} .

The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] showed a glass transition temperature of 70°C. The differential scanning calorimetry thermogram of poly[oxy-cis,trans-1,2-cyclohexyleneoxycarbonyl-cis,trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyisophthaloyl] showed a glass transition temperature of 63°C.

The ^{13}C NMR spectrum of the block copolymer was obtained in CDCl_3 . The ^{13}C chemical shifts and integrals were as follows: δ 10.2 (2.1), 20.8 (1.1), 21.7 (2.3), 23.2 (3.7), 24.6 (2.1), 25.2 (5.8), 26.2 (2.0), 27.7 (2.4), 29.0 (5.3), 30.0 (1.9), 34.8 (3.1), 42.7 (0.7), 44.8 (4.9), 60.2 (0.7), 60.8 (1.9), 71.2 (2.2), 75.8 (2.5), 120.1 (4.6), 123.9 (1.2), 126.9 (2.1), 129.4 (3.1), 130.1 (4.5), 131.9 (2.7), 135.2 (5.2), 150.2 (2.7), 163.7 (2.5), 172.7 (0.3), and 173.9 (2.2). The low-field peaks (δ 173.9, 172.7 and 163.7) correspond to carbonyl carbons. The resonances at δ 120.1-150.2 represent aromatic carbons and the resonances at δ 10.2-75.8 represent aliphatic carbons.

E. Preparation of Poly[oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (V).

A 500-mL three-necked, round bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 25.74g (0.2220 mol) of trans-1,2-cyclohexanediol and 120 mL of dry o-dichlorobenzene. To the stirred solution was added 42.08g (0.2000 mol) of trans-1,2-cyclohexanedicarboxoyl chloride in an atmosphere of nitrogen. The mixture was heated for 1.25 h at 115°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 7.5 h.

A 500-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 25.0g (0.200 mol) of 2-methylresorcinol and 180 mL of dry o-dichlorobenzene.

To this stirred solution was added 46.0g (0.2266 mol) of terephthaloyl chloride in an atmosphere of nitrogen. The mixture was heated for 1 h at 120°C. The mixture was then heated under reflux for 6.5 h.

After cooling, 60 mL of each of the two polyester solutions were mixed thoroughly in an atmosphere of nitrogen and heated under reflux for 1.5 h. The mixture was then heated for 8 h at 150°C. After cooling, the polymer was precipitated by pouring the reaction mixture into 500 mL of hexane. The polymer was allowed to stand in hexane for 1 day. After washing twice with acetone, three times with deionized water, and finally with acetone, 11g of polymer was obtained after drying in a vacuum oven for 48 h at 120°C.

The inherent viscosities for poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were 0.06 and 0.44 dL/g respectively, at 30°C in m-cresol. The in-

herent viscosity of the corresponding block copolyester, poly[oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] was 0.27 dL/g at 30°C in m-cresol.

Elemental analysis showed a number-average degree of polymerization of 5 for the poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $\text{H}(\text{C}_{14}\text{H}_{20}\text{O}_4)_5\text{C}_6\text{H}_{11}\text{O}_2 \cdot 2\text{H}_2\text{O}$: C, 64.59; H, 8.22. Found: C, 64.22; H, 8.13. Elemental analysis showed a number-average degree of polymerization of 17 for the poly[(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd for $\text{HO}(\text{C}_{15}\text{H}_{10}\text{O}_4)_{17}\text{C}_8\text{H}_5\text{O}_3$: C, 70.38; H, 3.93. Found: C, 70.20; H, 4.18.

The infrared spectrum showed peaks at 3400 (O-H stretch), 2910 and 2840 (aliphatic C-H stretch), 1720 (ester C=O stretch), 1450 (aromatic nucleus), and 1250, 1070, and 1005 (C-O stretch) cm^{-1} .

The differential scanning calorimetry thermogram of poly(oxy-trans-1,2-cyclohexyleneoxycarbonyl-trans-1,2-cyclohexylenecarbonyl) showed a glass transition temperature of 68°C. The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] showed a crystalline melting point of 313°C. The differential scanning calorimetry thermogram of the corresponding block copolyester showed a melting endotherm at 320°C.

The ^1H NMR spectrum of the block copolymer was obtained in CDCl_3 . The ^1H chemical shifts and integrals were as follows: δ 1.26 (1.0), 1.32 (3.1), 1.74 (3.1), 1.82 (0.2), 1.85 (0.7), 1.99 (1.9), 2.15 (1.8), 2.56 (0.8), 3.74 (0.4), 4.79 (1.1), 7.20 (0.3), 7.34 (0.2), 7.36 (0.2), 8.25 (0.3), and 8.38 (1.3). The resonances at δ 1.26-4.79 represent aliphatic protons, and the resonances at δ 7.20-8.38 represent aromatic protons.

F. Preparation of Poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) (VII)

The same procedure in E was followed. For the preparation of the cycloaliphatic oligomer, 28.70g (0.1373 mol) of trans-1,4-cyclohexanedicarboxoyl chloride, 17.56g (0.1510 mol) of trans-1,4-cyclohexanediol, and 190 mL of dry o-dichlorobenzene were used. For the preparation of the aromatic oligomer, 44.70g (0.2200 mol) of terephthaloyl chloride, 22.02g (0.2000 mol) of hydroquinone, and 240 mL of dry o-dichlorobenzene were used. After 100 mL of each solution were mixed, refluxed, and heated, 17g of VI was obtained by precipitation with acetone.

The inherent viscosity of poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) was 0.31 dL/g in o-chlorophenol at 30°C. Poly(oxy-1,4-phenyleneoxyterephthaloyl) was insoluble in o-chlorophenol. An inherent viscosity of 0.43 dL/g was obtained for poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) at a concentration of 0.4g/100 mL of o-chlorophenol at 30°C.

Elemental analysis showed a number-average degree of polymerization of 16 for the poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $H(14H_{20}O_4)_{16}C_6H_{11}O_2 \cdot H_2O$: C, 66.26; H, 8.02. Found: C, 66.16; H, 8.24. Elemental analysis showed a number-average degree of polymerization of 12 for the poly(oxy-1,4-phenyleneoxyterephthaloyl) oligomer. Anal. Calcd for $HO(C_{14}H_8O_4)_{12}C_8H_5O_3 \cdot H_2O$: C, 68.92; H, 3.39. Found: C, 68.72; H, 3.66.

The infrared spectrum of the block copolyester showed peaks at 3400 (O-H stretch), 2930 and 2850 (aliphatic C-H stretch), 1715 (ester C=O stretch), 1600 and 1490 (aromatic nucleus), and 1240, 1070, 1035, and 1010 (C-O stretch) cm^{-1} .

The ^1H NMR spectrum of the block copolyester was obtained in CDCl_3 . The ^1H chemical shifts and integrals were as follows: δ 1.26 (1), 1.51 (15), 1.65 (1), 1.72 (1), 1.84 (3), 1.91 (1), 1.95 (1), 2.05 (4), 3.73 (3), 8.09 (1), and 8.11 (1). The resonances at δ 1.26-3.73 represent aliphatic protons and the resonances at δ 8.09 and 8.11 represent aromatic protons.

Methylene chloride-o-chlorophenol solutions of poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxy-terephthaloyl) depolarized plane-polarized light when thin layers of the solutions were viewed at 504 X magnification.

G. Preparation of Poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] (IX).

The same procedure in E was followed. For the preparation of the cycloaliphatic oligomer, 25.5g (0.220 mol) of trans-1,4-cyclohexanediol, 41.8g (0.200 mol) of trans-1,4-cyclohexanedicarboxoyl chloride, and 300 mL of dry *o*-dichlorobenzene were used. For the preparation of the aromatic oligomer, 24.8g (0.200 mol) of methylhydroquinone, 44.7g (0.220 mol) of terephthaloyl chloride, and 300 mL of dry *o*-dichlorobenzene were used. After 150 mL of each solution were mixed, refluxed, and heated, 50g of IX was obtained by precipitation with acetone.

The inherent viscosities of poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] were 0.55 and 0.58 dL/g, respectively, in 3:1 (v/v) methylene chloridetrifluoroacetic acid at 30°C. The inherent viscosity for the corresponding block copolyester was 0.85 dL/g in 3:1 (v/v) methylene chloride-trifluoroacetic acid at 30°C.

Elemental analysis showed a number-average degree of polymerization of 20 for the poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) oligomer. Anal. Calcd for $\text{H}(\text{C}_{14}\text{H}_{20}\text{O}_4)_{20}\text{C}_6\text{H}_{11}\text{O}_2$: C, 66.56; H, 7.99. Found: C, 66.38; H, 8.36. Elemental analysis showed a number-average degree of polymerization of 10 for the poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] oligomer. Anal. Calcd for $\text{HO}(\text{C}_{15}\text{H}_{10}\text{O}_4)_{10}\text{C}_8\text{H}_5\text{O}_3 \cdot \text{H}_2\text{O}$: C, 69.60; H, 3.96. Found: C, 69.82; H, 4.35.

The infrared spectrum showed peaks at 2940 (aliphatic C-H stretch), 1740 (ester C=O stretch), 1410 (aromatic C-H deformation), and 1250 and 1080 (C-O stretch) cm^{-1} .

The ^1H NMR spectrum of the block copolyester was obtained in CDCl_3 . The ^1H chemical shifts and integrals were as follows: δ 1.26 (3), 1.66 (2), 1.85 (4), 2.03 (1), 2.07 (3), 2.20 (2), 2.29 (3), 2.30 (2), 4.9 (1), 5.22 (2), 6.95 (1), 7.02 (1), 7.22 (1), 7.29 (1), 8.13 (1), 8.18 (1), 8.33 (1), 8.35 (1), 8.37 (1), and 8.39 (3). The resonances at δ 1.26-5.22 represent aliphatic protons and the resonances at δ 6.95-8.39 represent aromatic protons.

The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in CDCl_3 . The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 21.5 (0.2), 27.9 (0.3), 28.2 (0.2), and 130.5 (0.4). The resonances at δ 21.5-28.2 represent aliphatic carbons. The resonance at δ 130.5 represents aromatic carbons. The resonances due to the carbonyl carbons were not observed due to the limited solubility of the block copolyester.

1,1,2,2-Tetrachloroethane-o-chlorophenol-phenol (60:25:15 v/v/v) solutions of poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] depolarized plane-polarized light when thin layers of the solutions were viewed at 100 X magnification. When the solutions were sheared by the movement of the cover slide, microdo-

mains of oriented, extended-chain segments were observed to form on microscopic examination between crossed polarizers.

H. Preparation of Poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X).

A 1-L three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a sodium hydroxide trap, was charged with 31.9g (0.275 mol) of trans-1,4-cyclohexanediol and 300 mL of dry o-dichlorobenzene. The mixture was heated to ca. 40°C, and to the stirred mixture was added 52.0g (0.249 mol) of trans-1,4-cyclohexanedicarbonyl chloride in an atmosphere of nitrogen. The mixture was heated for 0.5 h at 120°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 6 h. The reaction mixture was allowed to cool and stored in a desiccator overnight.

A 1-L three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a sodium hydroxide trap, was charged with 55.9g (0.276 mol) of terephthaloyl chloride and 300 mL of o-dichlorobenzene. The mixture was heated to ca. 40°C, and to this stirred mixture was added 31.0g (0.250 mol) of 2-methylresorcinol in an atmosphere of nitrogen. The mixture was heated for 1 h at 145°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 8 h. The solution was allowed to cool and stored in a desiccator overnight.

The two separately prepared polyester solutions (200 mL each) were mixed thoroughly in an atmosphere of nitrogen and heated for 1 h at 145°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 8 h in an atmosphere of nitrogen. After cooling, the polymer was precipitated by pouring the reaction mixture into hexane. The polymer was allowed to stand in hexane for 3 days. After washing once with acetone, twice with deionized water,

once with methanol, and finally with deionized water, 53.3g of polymer was obtained after drying in a vacuum oven for 48 h at 175°C.

Poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] homopolymers were isolated from the remaining solutions not used for block copolymerization by precipitation with acetone and hexanes, respectively. After washing and drying in the usual manner, 21.5g of poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) and 20.5g of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were obtained.

The inherent viscosities for poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] were 0.58 and 0.52 dL/g, respectively, at 30°C in o-chlorophenol. The inherent viscosity of the corresponding block copolyester, poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl], was 0.74 dL/g at 30°C in o-chlorophenol. Anal. Calcd for $(C_{14}H_{20}O_4)_n(C_{14}H_8O_4)_n$: C, 68.29; H, 5.69. Found: C, 67.96; H, 6.30. The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in $CDCl_3$. The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 10.2 (0.4), 27.7 (0.9), 28.1 (1.2), 42.8 (0.5), 70.5 (0.4), 120.2 (1.0), 123.8 (0.3), 127.0 (0.6), 130.6 (3.8), 133.8 (0.6), 150.3 (0.6), 163.8 (0.5), and 175.1 (0.2). The resonances at δ 10.2-70.5 represent aliphatic carbons. The resonances at δ 120.2-150.3 represent aromatic carbons. The low-field peaks (δ 175.1 and 163.8) correspond to carbonyl carbons. Table 1 shows the analysis of the C-13 NMR spectrum of block copolyester X.

TABLE I

C-13 NMR ANALYSIS OF X

| Model Compounds | | Polymer |
|-----------------|-----------------------|---------------|
| | | |
| ASSIGNMENTS | | |
| CARBON | MODEL COMPOUNDS (ppm) | POLYMER (ppm) |
| C-1 | 71.7 | 76.6 |
| C-2 | 28.2 | 27.7 |
| C-3 | 42.6 | 42.6 |
| C-4 | 28.3 | 28.1 |
| C-5 | 176.6 | 176.1 |
| C-6 | 9.8 | 10.2 |
| C-7 | 123.6 | 123.6 |
| C-8 | 166.2 | 160.2 |
| C-9 | 119.8 | 120.2 |
| C-10 | 126.9 | 127.0 |
| C-11 | 134.9 | 133.8 |
| C-12 | 129.6 | 130.6 |
| C-13 | 162.9 | 163.2 |

Table I C-13 NMR Analysis of X

The differential scanning calorimetry thermogram of poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] showed a crystalline melting point of 300°C. The differential scanning calorimetry thermograms of poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl) and the corresponding block copolyester (X) showed no transitions before decomposition.

Optical microscopy in cross-polarized light of 25% (w/w) solutions of poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) in o-chlorophenol resulted in the depolarization of plane-polarized light (Figure 4) when thin layers of the solutions were viewed at 158 X magnification. The photomicrographs of o-chlorophenol solutions of X resemble those of nematic-isotropic biphasic systems. The photomicrographs of the birefringent phase have the appearance of the threaded schlieren texture, which is characteristic of the nematic mesophase.

Isomerization Polymerization

The attempt to prepare poly[oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI) led to the preparation of poly[oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II).

Attempted Preparation of Poly[oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI).

A 250-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 11.4g (0.0983 mol) of cis-1,4-cyclohexanediol and 135 mL of dry o-dichlorobenzene. To the stirred solution was added 18.8g (0.0900 mol) of trans-1,4-cyclohexanedicarbonyl chloride in an atmosphere of nitrogen. The

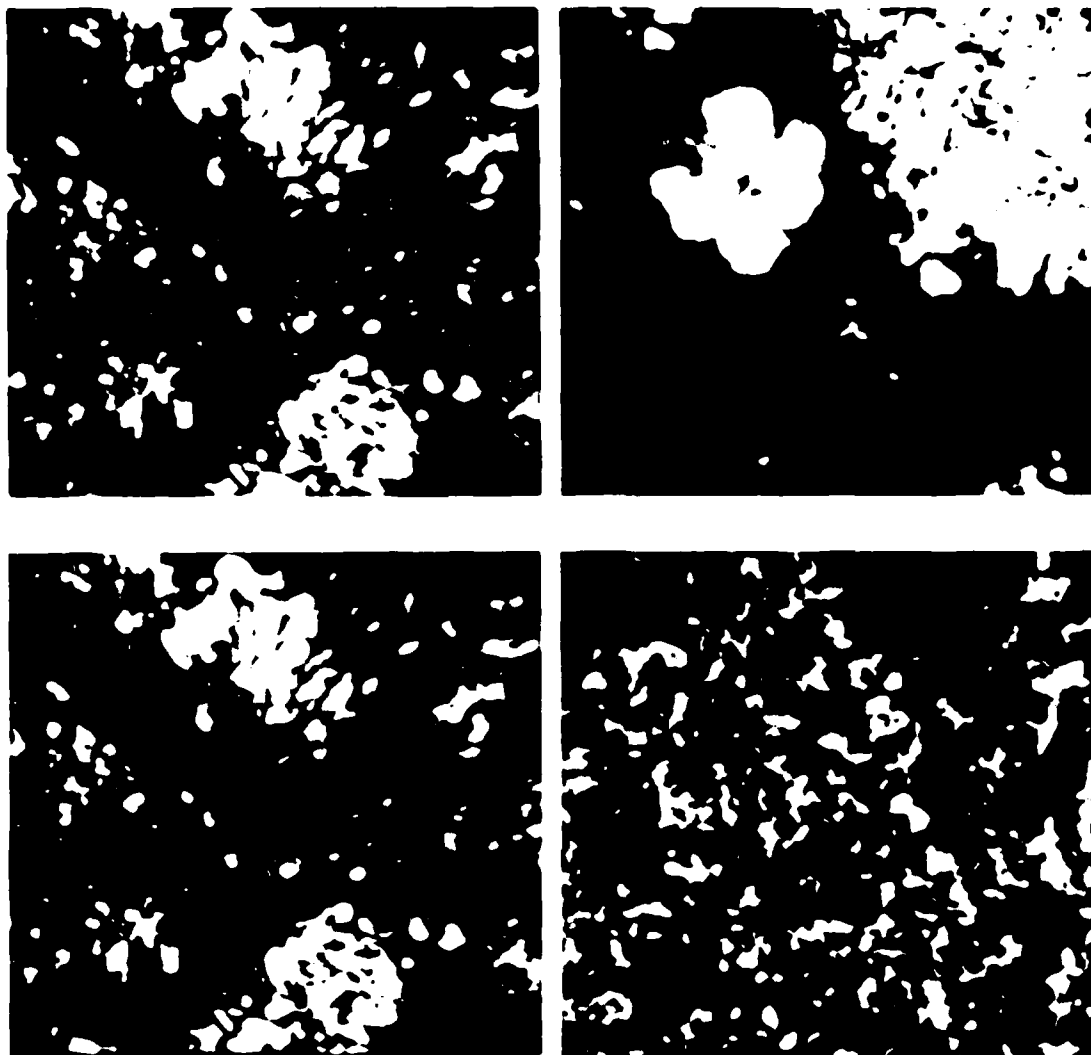


Figure 4. Optical Micrographs of X in 25% o-chlorophenol Solution in Cross polarized Light

mixture was heated for 1.5 h at 115°C, accompanied by the evolution of HCl. The mixture was then heated under reflux for 7.5 h.

A 250-mL three-necked, round-bottom flask, equipped with a magnetic stirrer, a condenser, a nitrogen inlet, a thermometer, and a potassium hydroxide trap, was charged with 11.2g (0.0903 mol) of 2-methylresorcinol and 135 mL of dry o-dichlorobenzene. To this stirred solution was added 20.1g (0.0991 mol) of terephthaloyl chloride in an atmosphere of nitrogen. The mixture was heated for 1 h at 120°C. The mixture was then heated under reflux for 9 h.

After cooling, 120g of each of the two polyester solutions was mixed thoroughly in an atmosphere of nitrogen and heated for 8 h at 145°C. After cooling, the polymer was precipitated by pouring the reaction mixture into 300 mL of acetone. The polymer was allowed to stand in acetone for 3 days. After washing twice with acetone, several times with deionized water, twice with methanol, and finally several times with deionized water, 26.5g of polymer was obtained after drying in a vacuum oven for 4 h at 115°C and 8 h at 175°C.

The homopolymers were isolated from the remaining solutions not used for block copolymerization by precipitation with acetone. After washing and drying in the usual manner, 9.0g of the cycloaliphatic homopolymer and 3.5g of the poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] oligomer were obtained.

Properties of the Product Obtained from the Attempted Synthesis of Poly[oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl].

The inherent viscosity for the aliphatic block copolyester oligomer was 0.16 dL/g at 30°C in o-chlorophenol. Poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] was found to be too insoluble in o-chlorophenol, m-cresol, and a 3:1 (v/v) methylene chloride-trifluoroacetic acid mixture for a determination of

inherent viscosity at 30°C. The inherent viscosity of the corresponding block copolyester was 0.38 dL/g at 30°C in o-chlorophenol.

The infrared spectrum showed peaks at 3440 (O-H stretch), 2930 and 2850 (aliphatic C-H stretch), 1720 (ester C=O stretch), 1450 (aromatic nucleus), and 1250, 1080, 1035, and 1005 (C-O stretch) cm^{-1} .

The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in CDCl_3 . The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 10.1 (0.4), 23.1 (0.2), 26.1 (0.2), 27.1 (0.2), 27.4 (4.8), 27.7 (5.2), 28.1 (12.2), 30.7 (0.1), 42.8 (5.1), 69.8 (2.3), 133.8 (0.3), 150.3 (0.3), 163.8 (0.2), 175.5 (0.6), and 175.1 (1.1). The resonances at δ 10.1-70.5 represent aliphatic carbons. The low-field peaks (δ 175.1, 175.0, and 163.8) correspond to carbonyl carbons.

Carbon-13 NMR Analysis

Analysis of the carbon-13 NMR spectra of the products of the attempted syntheses of block copolymers containing the oxy-cis-1,4-cyclohexyleneoxycarbonyl moiety indicated that the syntheses resulted instead in the preparation of block copolyesters containing the oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl moieties distributed along the chain.

A. Analysis of the Carbon-13 NMR Spectrum of Poly[oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II).

The carbon-13 spectrum of II is shown in Figure 5. Table II shows the assignments of the chemical shifts obtained for II. The model compounds for II included the same four used for the analysis of the spectrum of X and cis-1,4-cyclohexanediol diacetate (v). cis-1,4-Cyclohexanediol diacetate was prepared by the reaction of cis-1,4-cyclohexanediol with acetic anhydride.

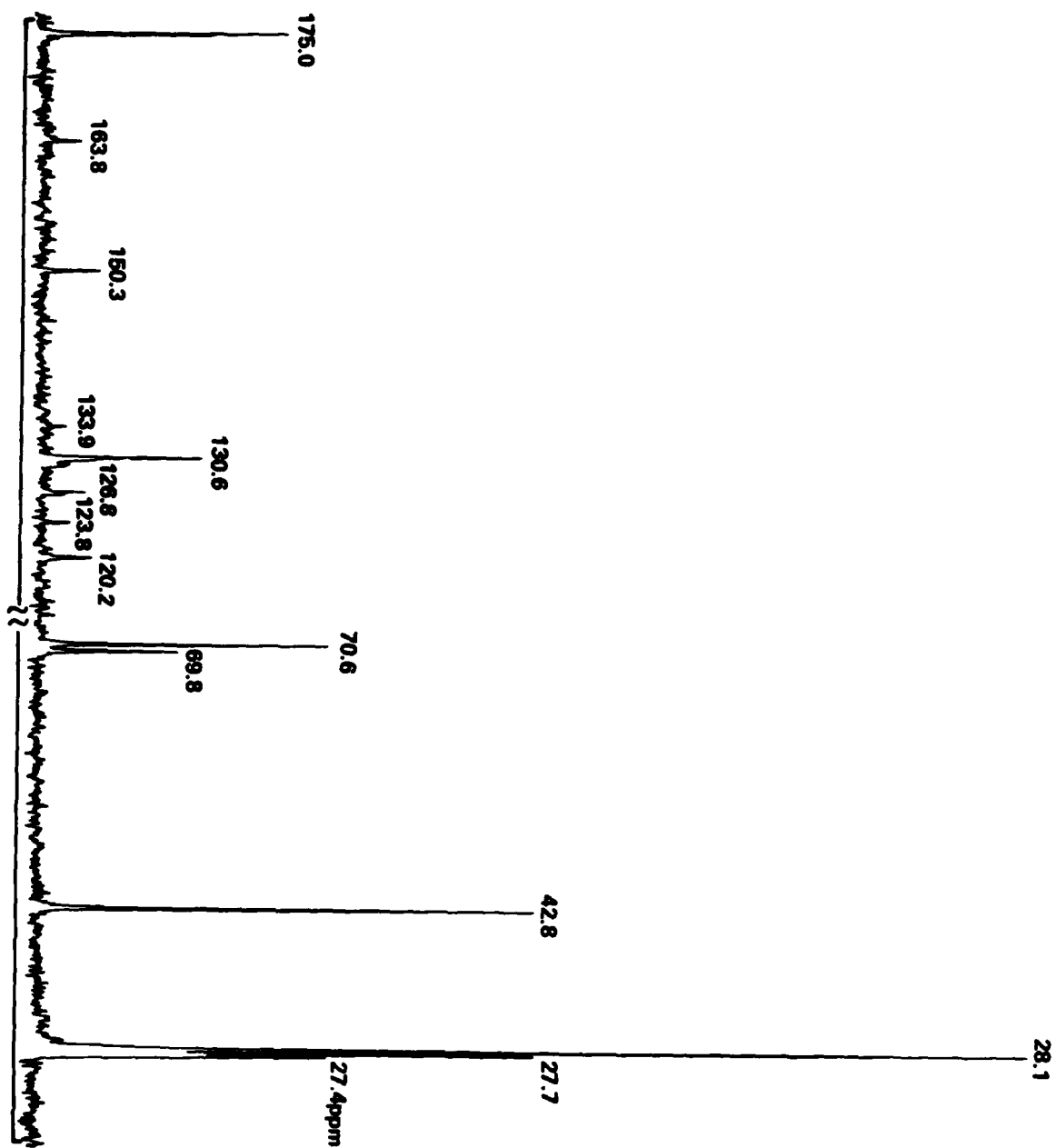
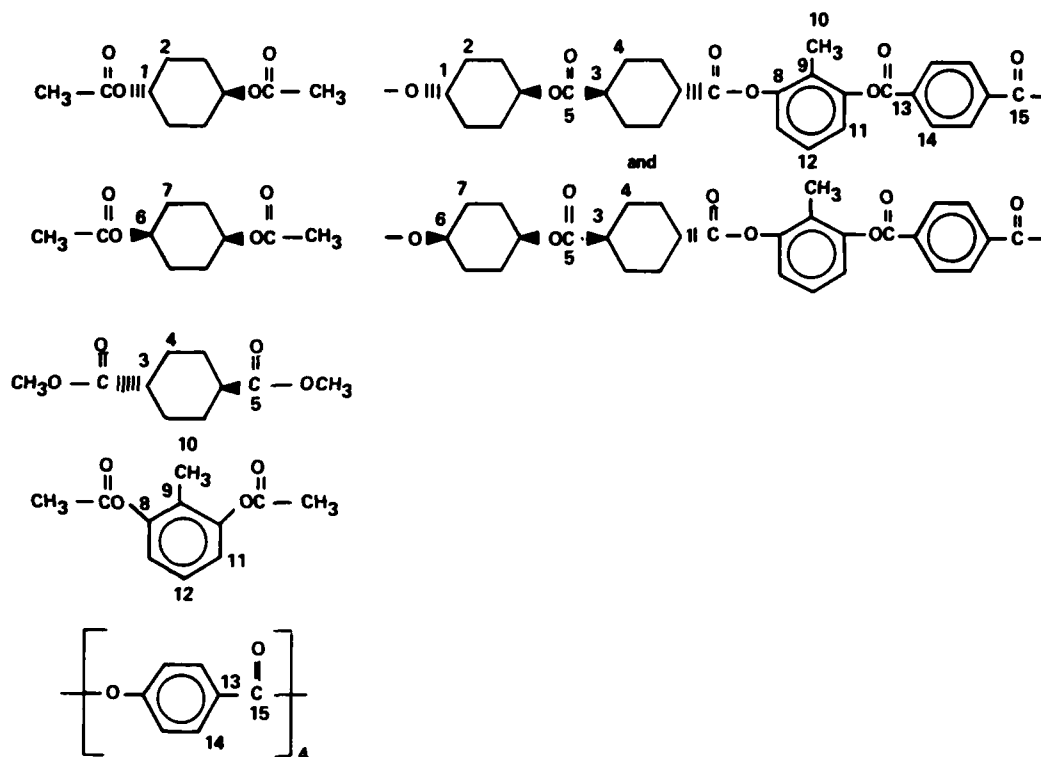


Figure 5. C-13 NMR Spectrum of 1j

Monomers



| ASSIGNMENTS | | |
|-------------|--------------------|---------------|
| | MONOMER (ppm) | POLYMER (ppm) |
| C-1 | 71.7 | 70.6 |
| C-2 | 28.2 | 27.7 |
| C-3 | 42.6 | 42.8 |
| C-4 | 28.3 | 28.1 |
| C-5 | 175.5 | 175.0 |
| C-6 | 70.1 | 69.8 |
| C-7 | 27.4 | 27.4 |
| C-8 | 150.2 | 150.3 |
| C-9 | 123.5 | 123.8 |
| C-10 | 9.8 | 10.1 |
| C-11 | 119.8 ^a | 120.2 |
| C-12 | 126.5 | 126.8 |
| C-13 | 126.0 | 126.8 |
| C-14 | 131.1 | 130.6 |
| C-15 | 162.9 | 163.8 |

The assignments were the same as those for X except the resonances at 69.8 and 27.4 ppm were assigned to the carbons α and β to the oxygen bonded to the cis-cyclohexylene ring, respectively.

B. Analysis of the Carbon-13 NMR Spectrum of the Product Obtained from the Attempted Synthesis of Poly[oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI).

The carbon-13 spectrum of the product of the attempted synthesis of XI is shown in Figure 6. Although the relative intensities of the peaks are different (especially in comparing the aromatic and cycloaliphatic regions) and in spite of the presence of small peaks at 23.1, 26.1, 27.1, and 30.7 ppm, which we attribute to impurities, the carbon-13 NMR spectrum is essentially the same as that of block copolyester II.

C. Analysis of the Carbon-13 NMR Spectrum of Poly[oxy(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenylene-terephthaloyl] (I). Block copolyester I was prepared by the method described in the literature. The inherent viscosity of the block copolyester was 0.48 dL/g at 30°C in o-chlorophenol. The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of the block copolyester was obtained in CDCl_3 . The ^{13}C chemical shifts (relative to Me_4Si) and integrals were as follows: δ 27.4 (1.2), 27.7 (1.7), 28.1 (3.5), 42.8 (1.6), 69.8 (0.8), 70.5 (1.0), 133.8 (0.7), 134.4 (0.6), 134.8 (0.7), 168.7 (0.1), 175.0 (0.1), 175.1 (0.4), and 183.3 (0.3). The resonances at δ 27.4-70.5 represent aliphatic carbons. The resonances at δ 133.8-134.8 represent aromatic carbons. The low-field peaks (δ 175.1, 175.0, and 168.7) correspond to carbonyl carbons.

The aliphatic region of the carbon-13 spectrum of block copolyester I at 300 K is shown in Figure 7. Table III shows that as expected the chemical

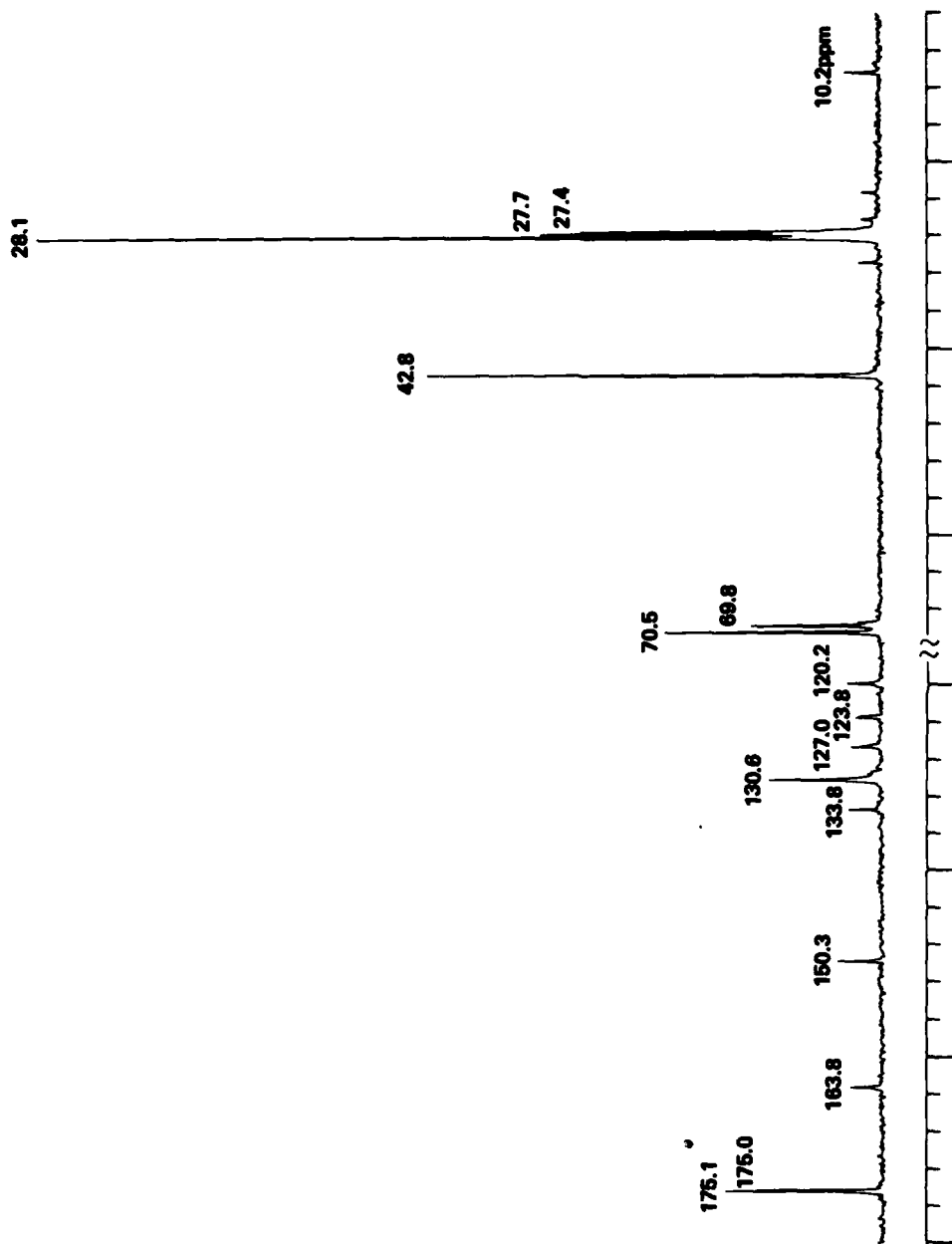


Figure 6. C-13 NMR Spectrum of Product of the Attempted Synthesis of VIII

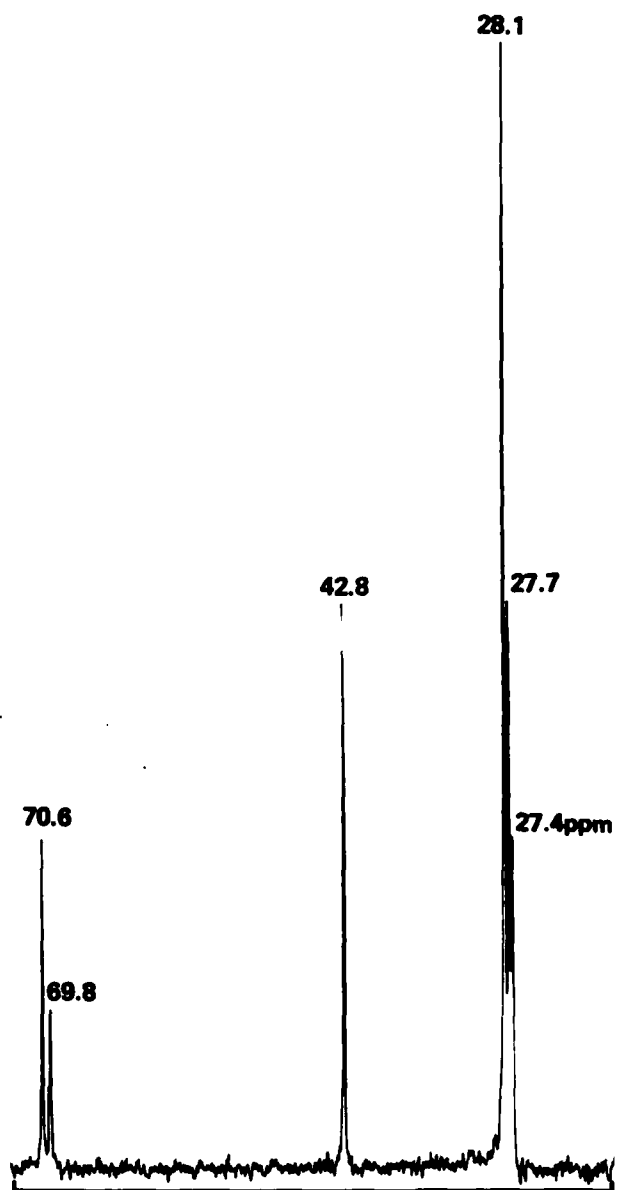


Figure 7. C-13 NMR Spectrum of Aliphatic Region of I

shifts for the aliphatic region of block copolyester I are the same as those for the aliphatic region of block copolyester II.

D. Analysis of the Carbon-13 NMR Spectrum of the Block Copolyester Assigned the Structure Poly(oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl- b-oxy-1,4-phenyleneoxyterephthaloyl) (VIII).

The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of block copolyester VIII was obtained in CDCl_3 . The ^{13}C chemical shifts (relative to Me_4Si) were as follows for the the aliphatic region: δ 27.4 (3.6), 27.7 (3.8), 28.1 (7.8), 42.8 (3.1), 69.8 (1.6), and 70.6 (1.8). Table III shows that the chemical shifts for the aliphatic region of block copolyester VIII are the same as those for the aliphatic region of block copolyester I.

Table III
Chemical Shifts for Aliphatic Regions of I, II, and VIII

| carbon | shift, ppm | | |
|--------|------------|------|------|
| | I | II | VIII |
| C-1 | 70.5 | 70.6 | 70.6 |
| C-2 | 27.7 | 27.7 | 27.7 |
| C-3 | 42.8 | 42.8 | 42.8 |
| C-4 | 28.1 | 28.1 | 28.1 |
| C-14 | 69.8 | 69.8 | 69.8 |
| C-15 | 27.4 | 27.4 | 27.4 |

The ^{13}C NMR results demonstrate that attempts to prepare block copolyesters containing poly(oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylene-carbonyl) blocks resulted in the formation of poly[oxy-(cis,trans)-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] blocks. In order to study this phenomenon, a ^{13}C NMR study of the monomers was initiated. Cis-1,4-cyclohexanediol (as obtained m.p. 91°C) and cis-1,4-cyclohexanediol recrystallized from acetone (m.p. $91-92^\circ\text{C}$) were analyzed by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the as obtained sample showed peaks at δ 30.5 (10.7), 32.9 (5.9), 67.7 (4.3), and 69.7 (2.5). According to the literature, the peaks at δ 30.5 and 32.9 (literature values were δ 31.3 and 33.9) represent the carbons β to the oxygen in the cis and trans isomers, respectively, and the peaks at δ 67.7 and 69.7 (literature values were δ 69.1 and 71.1) represent the carbons α to the oxygen in the cis and trans isomers. Therefore, the presumed cis-1,4-cyclohexanediol starting material was a mixture of the cis and trans isomers, with the cis isomer predominating.

The corresponding ^{13}C NMR resonances in block copolyester XI show that the trans configuration predominates in the polymer. The resonances and integrals corresponding to the carbons β to the oxygen in the polymer were δ 27.4 (4.8) and 27.7 (5.2) for the cis and trans isomers, respectively. The resonances and integrals corresponding to the carbons α to the oxygen in the polymer were δ 69.8 (2.3) and 70.5 (2.7) for the cis and trans isomers, respectively. Apparently, the greater thermodynamic stability of the trans-1,4-cyclohexane esters led to isomerization processes occurring during the polymerization of the predominantly cis-1,4-cyclohexanediol mixture and the resulting formation of a polymer with the predominantly trans-1,4-cyclohexylene configuration along the polymer backbone.

Characterization of the Polyesters

Thus far the only liquid crystal block copolyester which was soluble enough for a determination of molecular weight by GPC was poly(cis,trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) (Figure 8). The polymer had a number average molecular weight of 5,900 and a weight average molecular weight of 7,600. The molecular weight data were obtained on a hexafluoroisopropanol/sodium trifluoroacetate/water solution with a Waters 201 gel permeation chromatograph interfaced with a light scattering unit. A number average molecular weight of 5,900 is clearly too small for obtaining strong fibers and tough films. The inherent viscosity of the polymer was 0.41 dL/g. NMR analysis of the polymer in tetrachloroethane-d₂ solvent showed an aliphatic/aromatic block ratio of 3.1:1.0.

LARGE BATCH SYNTHESSES OF II, V, AND X

High molecular weight poly(cis,trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) II, poly(trans-1,4-cyclohexylene-trans-1,4-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) X, and poly(trans-1,2-cyclohexylene-trans-1,2-cyclohexanedioate-b-2-methyl-1,3-phenylene terephthalate) V have been synthesized and characterized.

We have prepared ca. fifty gram lots of all three polymers in reasonably high molecular weight. The inherent viscosities of I, II, and III were 0.74, 0.77, and 0.58 dL/g in *o*-chlorophenol at 30°C.

Mechanical property studies of block copolyesters II and X were abandoned after exhaustive solubility studies did not turn up a suitable solvent for solvent casting.

GEL PERMEATION STUDIES

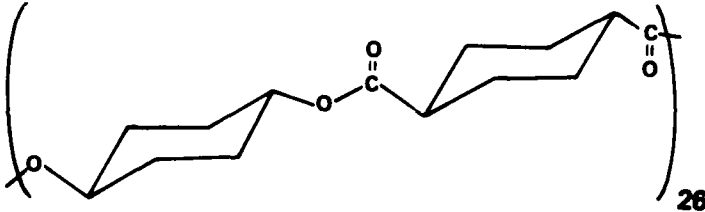
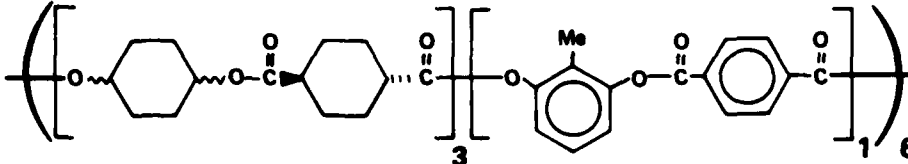
Purpose: Molecular Weight Information

Method: Gel Permeation Chromatography

Experimental Conditions Used for GPC Measurements

| | |
|-------------------------------|--|
| Instruments: | Water 201 |
| Columns: | Porous Silica (DuPont-4000, 1000 & 400) |
| Flow Rate: | 1.0 ml/min |
| Sample Volume Injected | 150 μ l |
| Concentration: | 0.2% wt/vol |
| Solvent: | HFIP. Sodium trifluoroacetate/H ₂ O |

Results: The number average molecular weight (\bar{M}_n), the weight average molecular weight (\bar{M}_w) and the molecular weight distribution ($MWD = \bar{M}_w/\bar{M}_n$) for the following samples were determined.

| <u>Sample</u> | <u>\bar{M}_n</u> | <u>\bar{M}_w</u> | <u>MWD</u> |
|--|-------------------------------|-------------------------------|------------|
| III - AL | 6,500 | 8,600 | 1.3 |
|  | | | |
| IV - B | 5,900 | 7,600 | 1.3 |
|  | | | |

Calculations were based on a calibration curve obtained with five PET molecular weight standards (the molecular weight range covered by these standards was 5000-31,500). Due to the difference between the type of polymer used as molecular weight standards and the sample polymers the reported information should be considered only as PET equivalent molecular weights.

Figure 8. GPC of II

CONCLUSIONS

In summary, we have prepared a number of liquid crystalline polyesters which contain cyclohexane and benzene rings. All of the lyotropic liquid crystalline polyesters prepared contained the trans-1,4-cyclohexylene-trans-1,4-cyclohexanediolate moiety. However although a number of these block copolyesters were shown to form lyotropic solutions, the presence of the cyclohexane rings severely affected the thermal limitations of the systems. Also we were unable to find suitable solvents for casting films of the liquid crystalline block copolyesters. Although poly(trans-1,2-cyclohexylene-trans-1,2-cyclohexanediolate-b-2-methyl-1,3-phenylene terephthalate) did not form lyotropic solutions, it was the only block copolyester which had a high enough molecular weight and low enough melting point (without decomposition) for melt spinning. However the fibers obtained were amorphous.

RECOMMENDATIONS

In order to decrease the melting points of the systems which we studied to below the decomposition temperatures, my recommendation would be to prepare random copolyesters which contain the cyclohexane and benzene rings in addition to flexible spacers. In this way thermotropic systems would be obtained with transition temperatures below the decomposition temperatures.

TECHNICAL REPORTS

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PERSONNEL

Principal Investigators: Malcolm B. Polk, Kofi B. Bota

Graduate Students: Edmond Akibuiro, James Ezike, Ngozi Abengowe, Metha

Phingbodhipakkiya, Ambrose Chukwuka, Charles Edeogu, Ogbuirubi Ibe-Uro, Mahendra Nandu, Marilyn Tate, Gabrielle Urguhart.

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- (3) Schaeffen, J.R.; Pletcher, T.C.; Kleinschuster, J.J. Belgium Patent 828 935, 1975.
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- (10) Schaeffgen, J.R. U.S. Patent 4 118 372, 1978.
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- (12) Jackson, W.J., Jr.; Kuhfuss, H.F. U.S. Patent 4 140 846, 1979.
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- (14) Jackson, W.J., Jr.; Bebeau, G.G.; Kuhfuss, H.F. U.S. Patent 4 153 779, 1979.
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- (16) Calundann, G.W. U.S. Patent 4 161 470, 1979.
- (17) Jackson, W.J., Jr.; Morris, J.C. U.S. Patent 4 169 933, 1979.
- (18) Jackson, W.J., Jr.; Morris, J.C. U.S. Patent 4 181 792, 1980.
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VOLUME 2. A PROPOSAL FOR A POLYMER RESEARCH CENTER AT THE
ATLANTA UNIVERSITY

INTRODUCTION

Goals and Objectives of the Polymer Research Center

The goals of the Polymer Research Center at the Atlanta University are to conduct the fundamental research and study of polymeric materials with respect to their synthesis, structure, physics and physical properties, and, in cooperation with other universities, industry and government laboratories and agencies, to elucidate their processing and engineering properties.

The objectives of the Center are:

- To conduct contract research and administer grants.
- To train and educate students at the M.S. and Ph.D. level through formal courses, seminars and workshops and research. The training and participation of students in research is considered a vital component of the Center's efforts and activities. In addition to carrying out specific experiments and study for their theses, students will be given a broad training in synthetic procedures and instrumentation techniques.
- To conduct or sponsor short courses for professionals who need an introduction to and continuing education about polymers.
- To serve as host during summers or sabbaticals to professors, especially from two- and four-year colleges, who need to have access to instrumentation for polymer research.
- To pursue cooperative arrangements with local universities. The faculty of Atlanta University participates in the monthly colloquium

on polymers held at the Georgia Institute of Technology. Under the auspices of the Polymer Research Center it is anticipated that a stronger relationship will be developed with the polymer group at Georgia Tech.

The activities of the Polymer Research Center in the academic year 1983-84 have included 1) a Physical Chemistry of Polymer Discussion Group conducted by Dr. George Collins of the Celanese Corporation, 2) a Polymer Chemistry course taught by Dr. Malcolm Polk, Director of the Center, as a regularly scheduled course, and visits by several consultants.

Table 1
Activities of the Polymer Research Center

| <u>Date</u> | <u>Participant</u> | <u>Activity</u> |
|-----------------------------------|---|---|
| Feb. 2, 1984- Feb. 3, 1984 | Dr. George Collins Celanese Corporation | Physical Chemistry of Polymers Discussion Group |
| March 12, 1984 | Dr. Mike Jaffe Celanese Corporation | Consultation Visit |
| March 22, 1984- March 23, 1984 | Dr. George Collins Celanese Corporation | Physical Chemistry of Polymers Discussion Group |
| March 30, 1984 | Dr. Edward Samulski Univ. of Connecticut | Seminar "Molecular Flexibility of Liquid Crystals" Consultation Visit |
| April 13, 1984 | Dr. David Dwight Virginia Polytechnic Institute | Seminar "Photoelectron Spectroscopy of Polymers" Consultation Visit |
| April 6, 1984- April 10, 1984 | Dr. Benjamin Taylor Univ. of Maryland | Consultation Visit |
| April 18, 1984- April 19, 1984 | Dr. George Collins Celanese Corporation | Physical Chemistry of Polymers Discussion Group |

The first Physical Chemistry of Polymers Discussion Group met on Feb. 2nd and 3rd for 2-two hour sessions based on Chapters 1 and 2 in "Thermodynamics of Polymerization" by Sawada. All of the Polymer Research Center principal investigators, postdoctoral associates, and a number of students were in attendance. We discussed the following concepts in depth: (1) ceiling temperature concept; (2) entropy and free energy changes; and (3) heats of polymerization. Several of the participants in the Polymer Research Center are also participating in the Polymer Discussion Group at Georgia Tech.

The Polymer Chemistry course, taught by Dr. Polk, was attended by ten students and the textbook is "The Elements of Polymer Science and Engineering" by Alfred Rudin. The scheduled topics for the course include: "Polymer Structure and Properties"; "Molecular Weights of Polymers"; "Step-Growth Polymerization"; "Chain-Growth Polymerization"; "Copolymerization," "Polymer Isomerism and Conformation" and "Mechanical Properties of Polymers."

As part of the Industrial Chemistry Seminar Series, the following seminars were presented by industrial polymer chemists: "Running a Polyethylene Pilot Plant" by Dr. Thomas Giacobbe (Mobil); "Polyurethane Automotive RIM" by Dr. Saad Abouzahr (Mobay); "Properties of Fiber Reinforced Composites" by Dr. David Garrett (General Motors); and "Physical Chemistry of Synthetic Lattices" by Jack Brodnyan (Rohm and Haas).

A general organization chart for the program is shown below:

Polymer Research Center

1984-85

Synthesis and Characterization (IR, NMR, GPC, TA)
(Banks, Polk, Mariam, Reed)

Summer 1984

Techniques in Physical Property Studies (SEM, X-Ray, Light-Scattering, DMA, Instron, Thermal Analysis - Bota, Collins, Korda, Olabisi)

1985-86

Synthesis and Characterization (IR, NMR, GPC, TA)
(Banks, Polk, Mariam, Reed)
Fabrication and Physical Property Testing
(Bota, Collins, Korda, Olabisi, Samulski)

1986-87

Synthesis and Characterization (IR, NMR, GPC, TA); Fabrication (films and fibers)
Physical Property Testing (SEM, X-Ray, Light-Scattering, Dynamic Mechanical Analysis, Tensile Testing, Thermal Analysis, Optical Microscopy).

Project #4

Synthesis and Characterization of Aromatic

Block Copolyesters

Principal Investigator: M. Polk

DESCRIPTION OF PROJECT

Our objectives were to prepare poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] I, (See Fig. 1) poly[oxy-2,2'-diphenyleneoxyterephthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl], and poly[oxy-2,2'-diphenyleneoxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl]. The following monomers were available commercially: 2-methylresorcinol; o,o'-diphenol; isophthaloyl chloride, and terephthaloyl chloride. The block copolyesters were to be prepared by the step-reaction polycondensation of the two polyester oligomers end-capped with hydroxy groups and terephthaloyl chloride. The oligomers were to be prepared by methods of step-reaction polycondensations of diols and diacid chlorides described elsewhere.

Routine analytical techniques such as infrared spectroscopy, proton and C-13 NMR spectroscopy, and elemental analysis were to be used to characterize the polymers while molecular weights were to be studied by employing such techniques as gel-permeation chromatography and light scattering analysis.

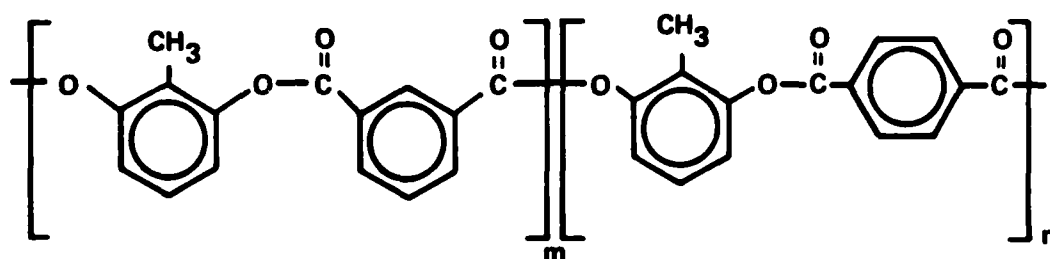


Figure 1. Structure of poly[oxy(2-methyl-1,3-phenylene) oxyisophthaloyl-b-oxy (2-methyl-1,3-phenylene) oxyterephthaloyl] I .

Optimization of Block Compositions

We proposed to optimize the solubility, thermal, and liquid crystalline properties of the block copolyesters by attempting to prepare block copolyesters with controlled ratios of the two blocks. For block copolyesters I, II, and III, we proposed to prepare polymers with block content ratios of 1:1 and 2:1 for the oxy(2-methyl-1,3-phenyleneoxyterephthaloyl) and the other block respectively. The block content ratios were to be monitored by ^{13}C NMR and gpc.

SIGNIFICANT RESULTS

Block copolyester I has been synthesized and characterized by infrared spectroscopy, proton and carbon-13 nuclear magnetic resonance spectroscopy, and solution viscosity.

Inherent viscosities were measured at 30°C in a 3:1 mixture of chloroform and trifluoroacetic acid at a concentration of 0.50g/dL. Carbon-13 NMR spectra were obtained in deuteriochloroform. Infrared spectra were obtained on KBr discs. Melting transitions were observed with a differential scanning calorimeter (DuPont 990 thermal analyzer with the DuPont 910 DSC accessory).

The inherent viscosity of block copolyester IA (1:1 ratio) was 0.40dL/g. The inherent viscosity of block copolyester IB (2:1 ratio) was 0.37dL/g. After modification of the two block copolyesters by reaction with additional terephthaloyl chloride the inherent viscosities of block copolyesters IA' and IB' were 0.58dL/g and 0.60dL/g, respectively.

The proton-decoupled carbon-13 NMR spectrum of IA is shown in Figure 2. The spectral assignments are shown in Table 1. We have tentatively assigned the peak at δ 9.1 to the end group methyl carbon and the peaks at δ 113.1 and 114.3 to carbons in the terminal aromatic rings.

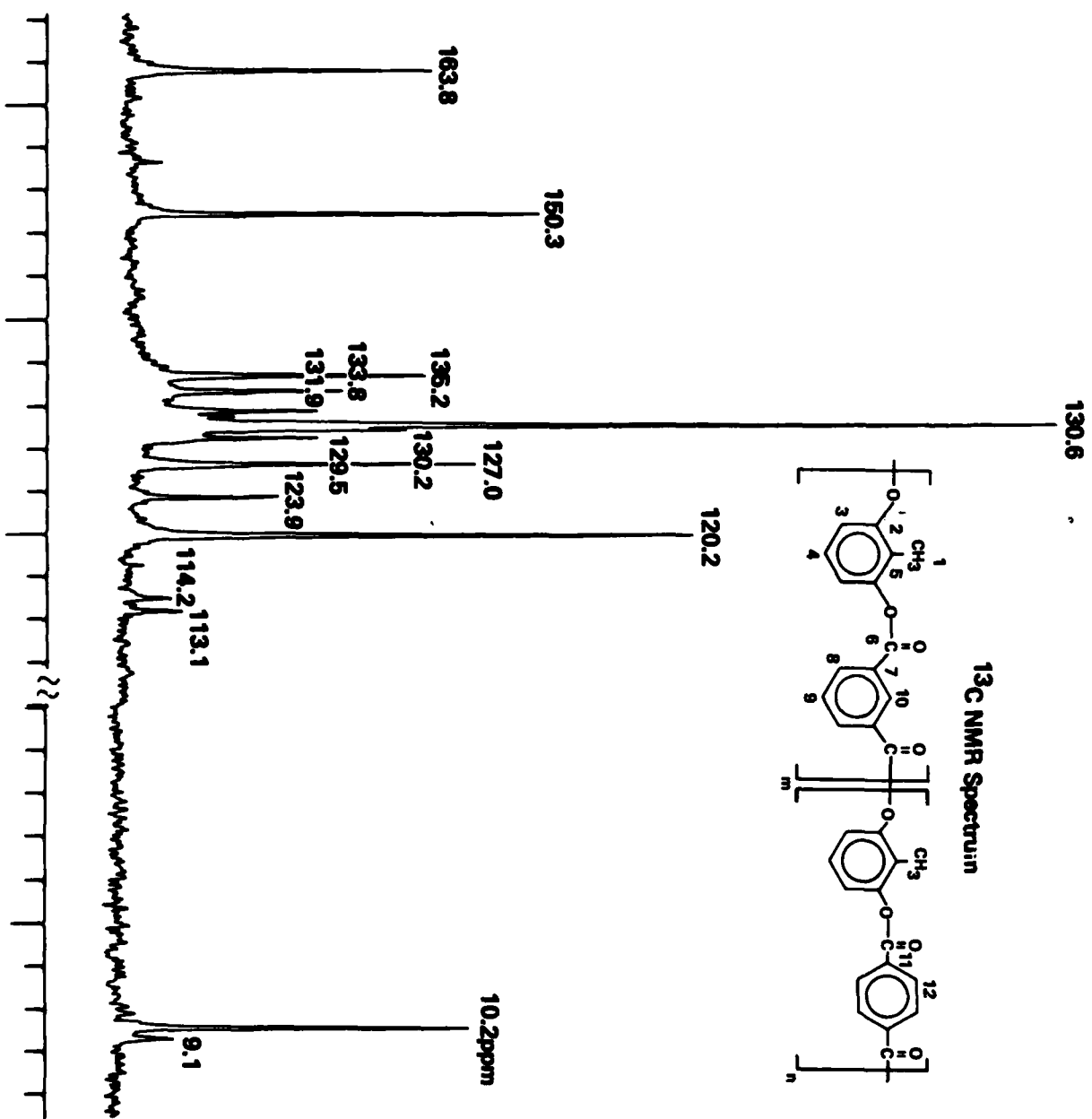


Figure 2

Table 1: Carbon 13 NMR Spectral Data for 1A.

| Carbon Number | Shift (ppm) | Integral |
|---------------|-------------|----------|
| 1 | 10.2 | 8.95 |
| 2 | 150.2 | 12.07 |
| 3 | 120.1 | 20.31 |
| 4 | 126.9 | 12.83 |
| 5 | 123.9 | 4.72 |
| 6 | 163.7 | 9.86 |
| 7 | 130.1 | 8.63 |
| 8 | 131.9 | 7.50 |
| 9 | 129.4 | 7.77 |
| 10 | 135.2 | 11.76 |
| 11 | 133.8 | 10.14 |
| 12 | 130.5 | 31.67 |
| 13 | 114.25 | 1.94 |
| 14 | 113.08 | 1.51 |
| 15 | 9.13 | 1.25 |

The DSC thermogram of IA shows a melting transition at ca. 330°C and no decomposition until well above 400°C. The DSC thermogram of IB shows a melting endotherm at ca. 328°C and no decomposition until above 400°C. The DSC thermogram of modified IB' shows, in addition to the melting transition at 343°C, an endotherm at 310°C. We have been able to pull reasonably tough fibers from the IB' polymer melt.

We have demonstrated that the endotherm at 310°C is not a crystalline to nematic liquid crystalline transition using polarizing optical microscopy. In fact, a color change from white to red occurs at that temperature. We are currently investigating the possibility of a reaction occurring at that temperature.

Block copolyesters II, III, IV, and V (Figures 3 and 4) have also been prepared. Block copolyester II was prepared by the reaction of poly(oxy-2,2'-diphenyleneoxyterephthaloyl) end-capped with hydroxy groups and poly[oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] end-capped with hydroxy groups with terephthaloyl chloride. Block copolyester III was prepared by the reaction of poly(oxy-2,2'-diphenyleneoxyisophthaloyl) end-capped with hydroxy groups and poly(oxy-2,2'-diphenyleneoxyterephthaloyl) end-capped with hydroxy groups with terephthaloyl chloride. Block copolyester IV was prepared by the reaction of poly(oxy-2,2'-diphenyleneoxyterephthaloyl) end-capped with hydroxy groups and poly[oxy(2-methyl-1,4-phenylene)oxyterephthaloyl] end-capped with hydroxy groups with terephthaloyl chloride. Block copolyester V was prepared by the reaction of poly(oxy-2,2'-diphenyleneoxyterephthaloyl) end-capped with hydroxy groups and poly[oxy(2-chloro-1,4-phenylene)oxyterephthaloyl] end-capped with hydroxy groups with terephthaloyl chloride.

The inherent viscosities of block copolyesters II, III, IV, and V were 0.531, 0.259, 0.559, and 0.564dL/g.

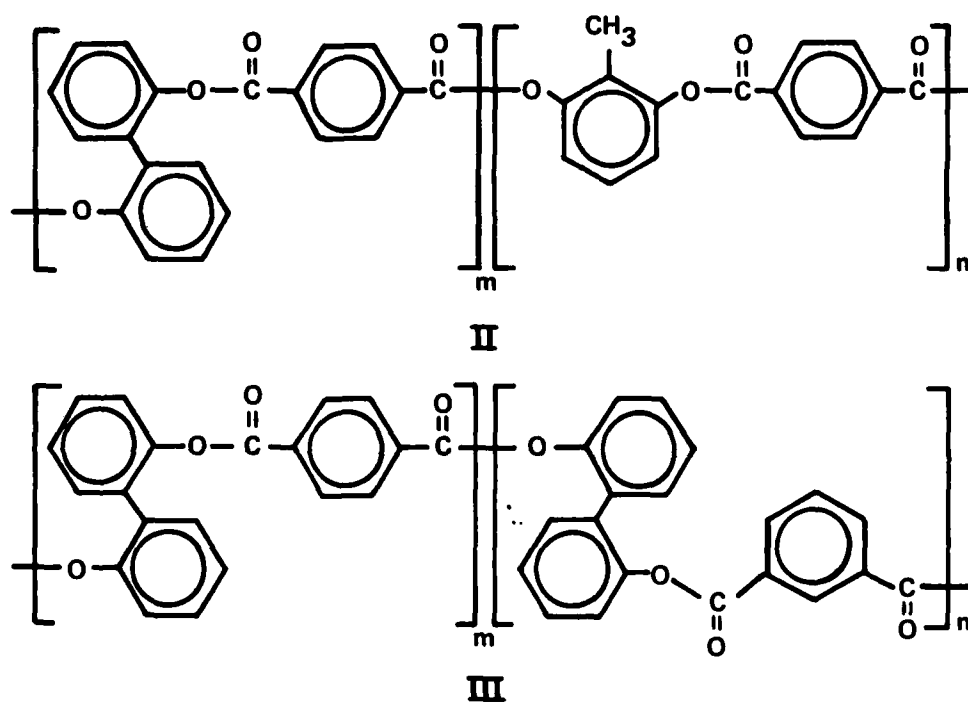


Figure 3. Structures of block copolymers II and III .

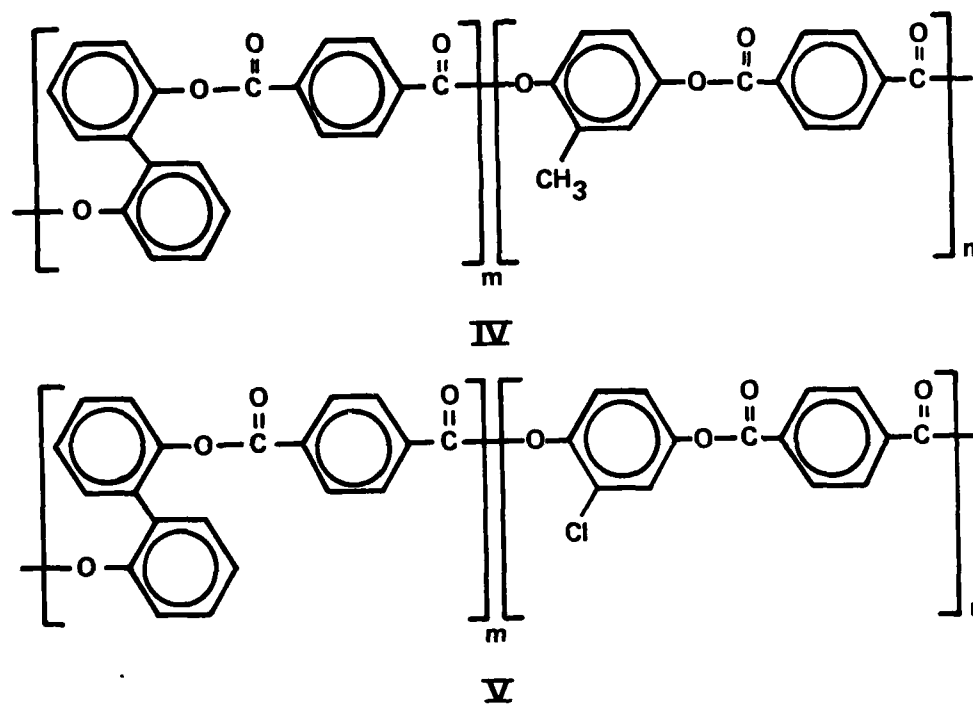


Figure 4. Structures of block copolymers IV and V.

The DSC thermogram of II shows transitions at 215°C, 275°C, and 328°C and no decomposition until well above 400°C. (See Figure 5). The DSC thermogram of V shows transitions at 158°C, 229°C, 275°C, and 345°C.

Thus far polarizing optical microscopy has not yielded any definitive liquid crystal textures for II, III, IV, or V, but we intend to continue our microscopic studies.

The proton-decoupled carbon-13 NMR spectrum of II showed peaks at δ 120.1 (0.8), 122.4 (1.7), 123.7 (0.2), 126.2 (1.5), 126.9 (0.5), 130.2 (1.1), 130.4 (3.9), 131.2 (2.4), 133.5 (1.2), 133.7 (1.1), 148.1 (1.0), 150.1 (0.7), 163.7 (0.7), and 163.9 (0.9).

CONCLUSIONS

We have prepared a number of all-aromatic block copolyesters, four of which contain the oxy-2,2'-diphenyleneoxyterephthaloyl moiety. Although the block copolyesters showed multiple peaks in the DSC which may represent thermotropic transitions, so far polarizing optical microscopy results are negative.

RECOMMENDATIONS

We recommend a more thorough polarizing optical microscopic analysis of these systems. Currently that work is underway.

PERSONNEL

Principal Investigator: Malcolm B. Polk
Graduate Students: Sheryl Brown, Issifu Harruna, Fidelis Onwumere
Technician: Metha Phingbodhipakkiya
Postdoctoral: Venu Kannappan

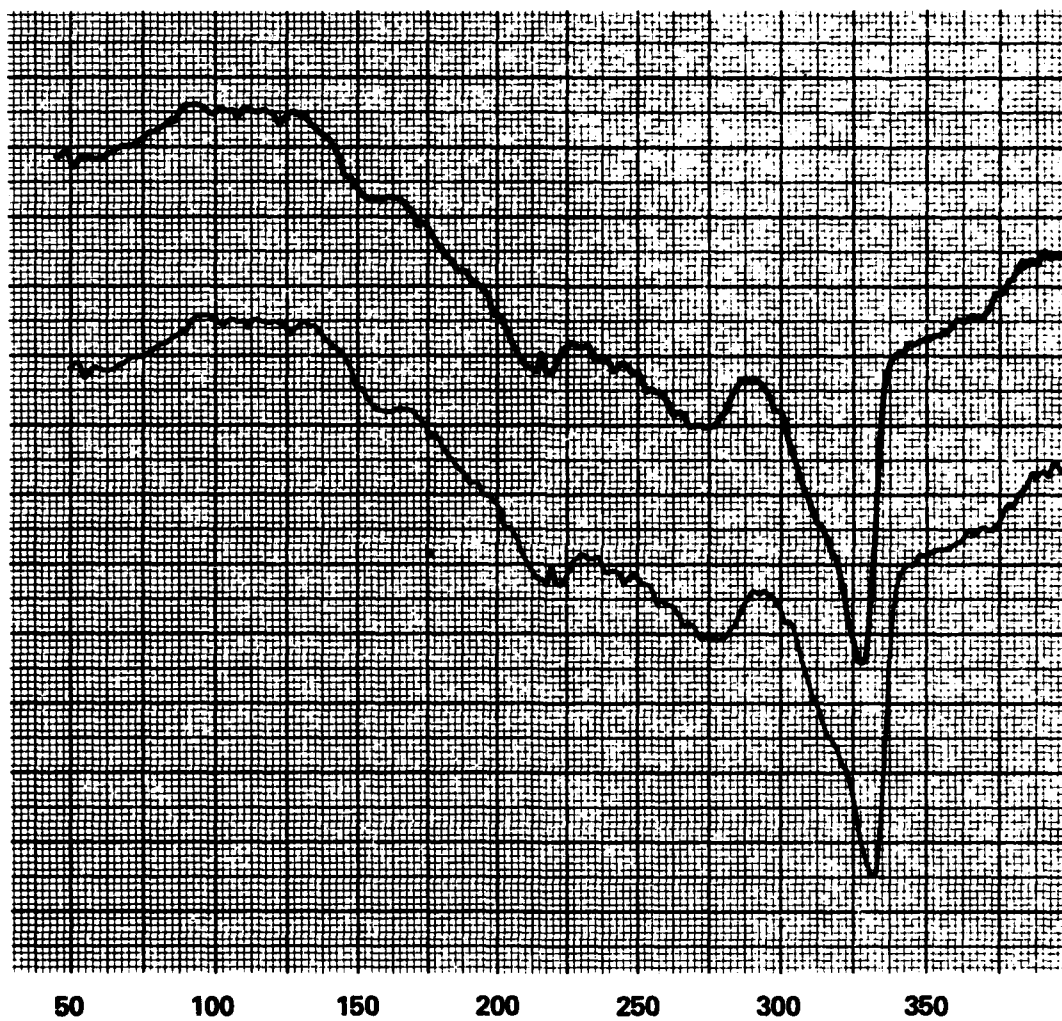


Figure. 5

PUBLICATIONS

Polk, M. B. and Onwumere, F. "The Synthesis and Characterization of Poly[oxy(2-methyl-1,3-phenylene)oxyisophthaloyl-b-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] accepted for publication by the Journal of Macromolecular Science.

Activities to Generate Other Resources:

Three proposals are under review

1. "Synthesis and Characterization of Liquid Crystalline Copoly(ester amides)"
Principal Investigators: M. Polk and H. Banks
Source: NASA
Requested Amount: \$750,000
Period: 10/1/84 - 9/31/87
2. "Study of the Molecular Structure and Physical Properties of Polymers"
Principal Investigator: M. Polk
Leo Raphaelian, Argonne National Lab
Source: DOE
Requested Amount: \$711,310
Period: 9/1/84 - 8/31/87
3. "Synthesis and Characterization of Polymeric Materials Based on Monomers Extractable" from Coal Tar"
Principal Investigators: M. Polk
V. Kannappan, Presidency College
Madras, India
Source: USAID
Requested Amount: \$150,000
Period: 9/1/84 - 8/31/86

Project #2

Synthesis of Monomers for the Preparation of
Low Temperature Thermotropic Polyesters

Principal Investigators: H. Banks and M. Polk

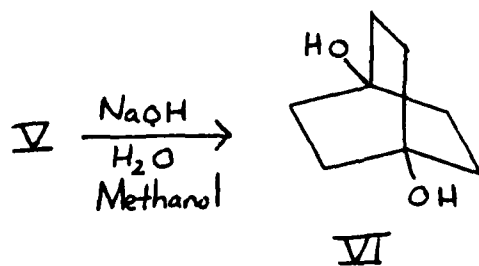
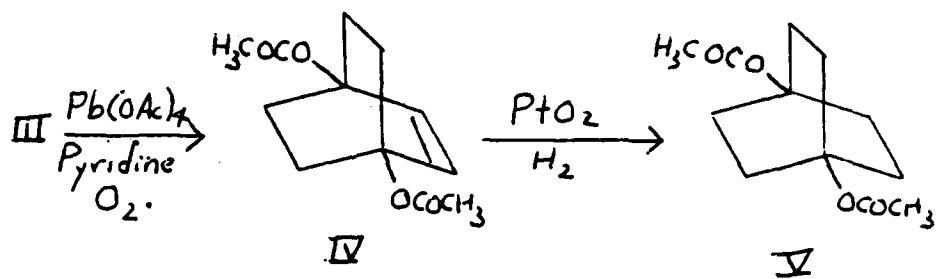
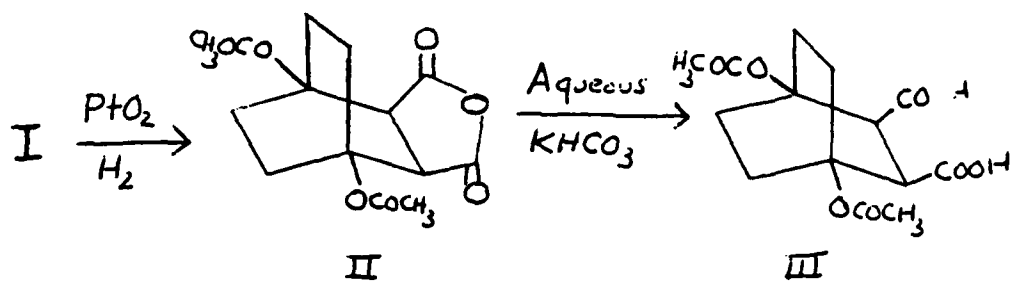
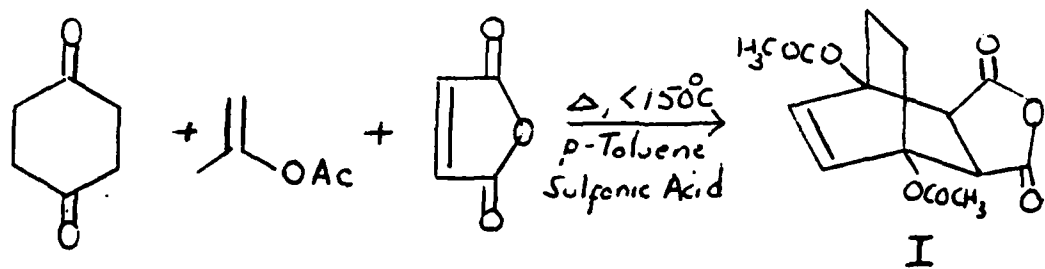
DESCRIPTION OF PROJECT

The syntheses of bicyclo[2.2.2]octane-1,4-dicarboxylic acid, 4-hydroxy-bicyclo[2.2.2]octane-1-carboxylic acid, and 1,4-dihydroxybicyclo[2.2.2]octane have been reported. We proposed to develop more efficient methods for the preparation and purification of these monomers for subsequent polymerization studies.

Some recent and new approaches to the synthesis of bicyclo[2.2.2]octane-1,4-dicarboxylic acid and bicyclo[2.2.2]octane-1,4-diol are being investigated.

A. Synthesis of Bicyclo[2.2.2]octane-1,4-diol

The general synthesis outlined by Kopecky et al¹ was followed with some modifications. The scheme envisaged for the synthesis is as follows:



SIGNIFICANT RESULTS

The first three steps of the synthesis leading to 1,4-diacetoxibicyclo[2.2.2]octane-2,3-dicarboxylic acid (III) here been performed and the reaction conditions standardized.

I. 1,4-Diacetoxibicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic acid anhydride (I)

The synthetic procedure was essentially adopted from those described in literature 1,2.

A mixture of 11.2 gms (0.1 mole) of 1,4-cyclohexanedione, 33ml of isopropenyl acetate (0.30 mole) and 10.8 gm of maleic anhydride (0.11 mole) was heated in the presence of 50-100 mg of p-toluenesulfonic acid monohydrate crystals.

The temperature was controlled to be less than 150°C and the heating was continued for 72 hours. Acetone was evaporated off using a roto-vap and the dark mixture was taken up in ethyl acetate and eluted through a neutral alumina chromatographic column using ethyl acetate as the eluent. The ethyl acetate extracts were concentrated using a roto-vap and hexane was added in drops till a turbidity first appeared. The solution was warmed till it disappeared and the solution was allowed to cool to room temperature. The white solid that separated out was filtered at the pump and washed with cold hexane-ethyl acetate mixtures. The solid was dried and its melting point was determined (206-208°C).

The yield was 9 grams (30%)

$^1\text{H-NMR}$ spectrum $(\text{CD}_3)_2\text{SO}$, δ , ppm:

1.7-2.6[m, 4H, $-\text{CH}_2-$]

2.1[s, 6H, CH_3-]

4.3[s, 2H, C-H]

6.4[s, 2H, $-\text{CH}=-$]

IR spectrum (KBr):

1790, 1780, 1755, 1735, 1370

1230, 1080, 920 cm^{-1}

II. 1,4-Diacetoxycyclo[2.2.2]octane-2,3-dicarboxylic Acid Anhydride (II)

This was prepared by the catalytic hydrogenation of I adopting the procedure described in literature for the hydrogenation of 1-carbomethoxy-2-endo-carbomethoxycyclo[2.2.2]octane-5,6-endo-dicarboxylic anhydride.³ 3g of I (0.01 moles) was dissolved in 50ml THF (Fisher Scientific, spectranalyzed grade) and the solution was hydrogenated in a Parr Hydrogenator at 40 psi hydrogen pressure. A rapid consumption of hydrogen took place as registered by the gauge (15-30 minutes). The bottle was shaken for 4-5 hours till no further fall in pressure was noticed. The pressure was gradually released, the reduced catalyst was filtered out and the filtrate was evaporated using a roto-vap leaving behind a pleasant smelling white solid. It was recrystallized from minimum quantities of acetone. Yields were quantitative (100%), melting point 183-184°C.

III. 1,4-Diacetoxycyclo[2.2.2]octane-2,3-dicarboxylic Acid (III)

This was prepared by the aqueous KHCO_3 hydrolysis of II. 2.5 grams of II were mixed with 11-12 ml of 20% KHCO_3 and heated under reflux till complete dissolution. The clear solution was allowed to cool to 4-5°C and concentrated HCl was added in drops till the medium turned sharply acidic as shown by pH indication. The mixture was kept in the cold room for 1-2 hours till complete precipitation occurred. The white solid was filtered at the pump. A part of it was recrystallized from 50% acetic acid and the melting point was determined (188°C). The yield was 1 gram (40%).

IV. Synthesis of Bicyclo[2.2.2]octane-1,4-diol

The synthetic route to bicyclo[2.2.2]octane-1,4-diol starting from 1,4-cyclohexanedione, isopropenyl acetate and maleic anhydride¹ was completed.

While the absolute yield of product was modest (0.5g), these experiments were necessary to optimize the conditions for synthesis of larger quantities of the diol for elaboration into polyesters.

V. Synthesis of Bicyclo[2.2.2]octane-1,4-dicarboxylic Acid

Bicyclo[2.2.2]octane-1,4-dicarboxylic acid has been prepared in reasonably good yield by the method of Wood.² Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.00. Found: C, 60.60; H, 6.99.

VI. Synthesis of Chiral Bicyclo[2.2.2]octanes

A. High Pressure Study

The preparation of 2-phenylsulfonyl-1,4-dicarbomethoxybicyclo[2.2.2]oct-5-ene by the reaction of 1,4-dicarbomethoxy-1,3-cyclohexadiene and phenyl vinyl sulfoxide on 5 mmolar scale at high pressure (10 Kbar) is being run at Merck Sharp & Dohme to test the feasibility of this type of approach to the synthesis of a Diels-Alder adduct of an electron-deficient diene. If this synthesis is successful, both the double bond and the sulfoxide group of the product (a mixture of diastereomers) will be reduced. Two recent reports^{3,4} for asymmetric oxidation of sulfides to sulfoxides give us confidence that the preparation of optically active 2-phenylsulfonylbicyclo[2.2.2]octane can be effected.

B. Use of 1,2-Bis(phenylthio)ethylene

Catalyzed ($AlCl_3$) and uncatalyzed reactions of 1,4-dicarbomethoxy-1,3-cyclohexadiene with 1,2-bis(phenylthio)ethylene at room temperature and atmospheric pressure are in progress. HPLC conditions for analysis of the product mixture have been determined. Optically active derivatives will be prepared as described above.

CONCLUSIONS

1. We have prepared bicyclo[2.2.2]octane-1,4-diol and bicyclo[2.2.2]octane-1,4-dicarboxylic acid in modest amounts.
2. We are proceeding with the synthesis of chiral bicyclo[2.2.2]octane derivatives and the development of more efficient procedures for the synthesis of the monomers.

PERSONNEL

Principal Investigators: Harold D. Banks and Malcolm B. Polk
Graduate Students: Mahendra Nandu, Fidelis Onwumere, Sheryl Brown
Technician: Metha Phingbodhipakkiya
Postdoctoral: N. Venkatasubramanian

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3. Pitchen, P.; Kagan, H. B. Tetrahedron Lett., 1984, 25, 1049-1052.
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Project #1

Preparation of Low Temperature Thermotropic Polyesters and Copolyesters

Principal Investigators: M. Polk and H. Banks

INTRODUCTION

We proposed to prepare poly[oxy-1,4-bicyclo[2.2.2]octyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl] I; poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl] II; poly[oxy-1,4-bicyclo[2.2.2]octyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl] III; poly[oxy-1,4-bicyclo[2.2.2]octyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-2-methyl-1,3-phenylene terephthalate] IV; poly[oxy-1,4-bicyclo[2.2.2]octyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy-trans-1,4-cyclohexyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylene carbonyl] V and poly[oxy-1,4-bicyclo[2.2.2] octylenecarbonyl] VI for subsequent liquid crystal studies.

RESULTS

Using the bicyclo[2.2.2]octane-1,4-dicarboxylic acid prepared in Project 2, we have prepared poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl], poly[oxy(2-methyl-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl], poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-chloro-1,4-phenylene)oxysebacoyl], poly[oxy(2-methyl-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-methyl-1,4-phenylene)oxysebacoyl], poly(oxy-trans-1,4-cyclohexyleneoxy-

carbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl) and poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy-trans-1,4-cyclohexyleneoxysebacoyl). Random copolyesters, poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-chloro-1,4-phenylene)oxysebacoyl], poly[oxy(2-methyl-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-methyl-1,4-phenylene)oxysebacoyl], and poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy-trans-1,4-cyclohexyleneoxysebacoyl) formed fluid birefringent states in the melt. We are currently in the process of preparing manuscripts for the publication of these results.

PERSONNEL

Principal Investigators: Harold D. Banks and Malcolm B. Polk
Graduate Students: Mahendra Nandu, Fidelis Onwumere, Sheryl Brown
Technician: Metha Phingbodhipakkiya
Postdoctoral: N. Venkatasubramanian

Project #9

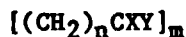
Synthesis of Active Moiety Containing Polymers

Principal Investigator: J. Reed

DESCRIPTION OF PROJECT

It was proposed that a number of new polymers be synthesized and characterized. In addition, these syntheses were carried out in such a manner as to systematically vary several aspects of the polymer structure. The objective was to improve known synthetic methods and where appropriate develop new synthetic methods. In addition this study was designed to yield new structure property relationships. The structural features which were systematically varied are: the backbone structure and polarity, the polymer chain length and the pendant active moiety.

Of the various types of polymer backbones available for study, this investigation focused on those derived at least structurally from polyethylene.



Because the active moieties are electrically charged, the polarity of the backbone is of special interest. This may be systematically varied by varying the substituents, X and Y. For the hydrophobic non-polar matrix, X and Y may be hydrogens or phenyl groups. For a hydrophilic polar matrix the substituents may be hydroxyl groups. Additionally, the polarity may be varied by changing the value of n.

In any systematic study of polymer properties, the molecular weight of the polymer must be controlled and systematically varied. Thus polymers ranging in

size from oligomers to high polymer were to be prepared. The pendant active moieties were to be model compounds which are isomorphous with various species of interest. They were to be of the tetradentate macrocyclic type to ensure structural integrity. The charge was to be varied by the appropriate choice of ligand or metal. Both kinetically labile and inert metals were to be used.

INTRODUCTION

The current phase of this investigation is concerned primarily with synthetic chemistry. We have been concentrating on the derivatization of three commercially available polymers. These are: polystyrene, polyvinyl alcohol and polyvinyl chloride.

EXPERIMENTAL

Polystyrene (M.W. = 30,000) - was obtained from Polysciences and used as is. Chloromethylether - was obtained from Aldrich and distilled three times before use.

Chloromethylated Polystyrene - 6g of polystyrene was dissolved in 90ml of chloromethylether and shaken with freshly fused and ground ZnCl_2 for one hour. An additional 1.4g of ZnCl_2 was added and the reaction allowed to continue for an additional five hours. This was followed by precipitation with methanol.

Iodomethylated Polystyrene - 2.5g chloromethylated polystyrene was dissolved in 40mL of acetone-dioxane (3:1; v/v) to which was added 1.5g NaI. This was refluxed for two days. The product was precipitated with water and dried.

(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-n-methylpolystyrene(tet-b).

Method I - 1.0g iodomethylated polystyrene and 0.5g tet-b were refluxed in

tetrahydrofuran for four days. The product was filtered and extracted with tetrahydrofuran.

Method II - To a solution of 6.5g naphthalene in 100mL tetrahydrofuran was added 0.7g of lithium metal. After one hour tet-b was added and stirred for an additional two hours. The chloromethylpolystyrene was then added and stirred for an additional hour. The reaction mixture was decomposed and the product filtered.

Method III - 0.355g chloromethylated polystyrene (MW = 30,000 for parent polystyrene) and 0.1877g tet-b • H₂O were dissolved in 30mL of tetrahydrofuran. This solution was placed in a 8.5 cm diameter evaporating dish and the solvent was allowed to evaporate. The resulting film was clamped between two teflon plates and heated at 90°C. The film was extracted for two hrs with tetrahydrofuran.

Poly(vinyl-p-toluenesulfonate) - 4.5g of polyvinyl alcohol and 50mL pyridine was heated in a steam bath for two hours. To this was added 100mL of pyridine and cooled to °C. Then 23.5g of p-toluene sulfonyl chloride was added and stirring continued for four hrs. An equal volume of acetone was added and the product precipitated in water.

The conversion of polyvinyl alcohol to poly(vinyl-p-toluene sulfonate) was attempted. When precipitation with water was attempted little precipitate forms which indicates little conversion to the hydrophobic product.

Dichloro(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-cobalt (III)-N-methylpolystyrene(Co-(tet-b)Cl₂)

Method I - 0.4g of cobaltous chloride hydrate was dehydrated on a hot plate and cooled in a desicator. This was added to 0.80g of tet-b swollen in tetrahydrofuran and refluxed under nitrogen for three days. The product was

permitted to undergo air oxidation and precipitated with hexanes and dried under vacuum.

Method II - 0.021g of dried polymer film (chloromethylated polystyrene treated with tet-b) and 0.1g CoCl_2 were refluxed for 2 1/2 hours at 95°C in 1:2 tetahydrofuran-N,N-dimethylformamide. The blue-green film was then extracted with tetahydrofuran for three hours.

RESULTS AND DISCUSSIONS

Polystyrene (NW = 30,000) was the first commercial polymer to be studied. The commercial polymer was converted to the chloromethylated polymer by treatment with chloromethylmethylether and zinc chloride.

This method was chosen because it is reported to result in no crosslinking in the final product. The product was readily soluble and exhibited a melting range of 148 - 150°C. The modest increase in melting point from (120°C to 148 - 150°C) and the high solubility suggests that there was little if any crosslinking. The calibration of the gel permeation chromatography has been completed and molecular weight determinations are underway. This polymer contains 23.43% chlorine which compares favorably to that expected for complete conversion to the chloromethylpolystyrene ($\text{Cl \%} = 23.30\%$ for $\text{C}_9\text{H}_9\text{Cl}$).

Attempts to convert this polymer to the polyamine by converting the chloromethyl polymer to the iodomethyl polymer followed by reaction with tet-b resulted in low yields. A more successful route consists of treatment of tet-b with a molar excess of naphthalide and reacting the polymer with the unisolated product. Results described in the next paragraph suggests that this conversion is also complete.

After isolation this product could not be completely dissolved in any solvent. This is not unexpected, because there is the possibility of crosslinking in a tetraamine and because hydrogen bonding will make dissolving the polymer difficult. The polymer did swell extensively in a number of solvents.

In order to metallate the polyamine it was swollen in tetrahydrofuran and treated with CoCl_2 under nitrogen. The inert atmosphere was necessary in order to prevent premature oxidation of cobalt, and to prevent the formation of aquo complexes. The product was green-brown. The $\text{Co}(\text{tet-b})\text{Cl}_2^+$ complex is also green but because the product was insoluble in all solvents tried thus far, optical data was not obtained. Attempts to obtain solid state transmission spectra were difficult because of the presence of the trail of an intense ultraviolet absorption band. The cobalt content of this polymer was determined by complete digestion in hot sulfuric acid and hydrogen peroxide, followed by reduction with hydroxylamine. Cobalt was then determined spectrophotometrically using the thiocyanate method. This polymer contained 10.5% cobalt. This compares favorably to 10.4% computed for $(\text{p-styrene-H})\text{-CH}_2\text{-(tet-b)CoCl}_3$, where (P-styrene) stands for polystyrene, and suggests complete conversion of the commercial polymer to $(\text{P-styrene-H})\text{-CH}_2\text{-(tet-b)CoCl}_3$. This polymer was extracted extensively with tetrahydrofuran. The extracts were colorless suggesting that cobalt is not lost. Analysis of the product yielded 11.7% ($\pm 6\%$) which indicates that primarily non-cobalt containing material was extracted from the polymer. If, however, the polymer was treated with boiling tetrahydrofuran containing lithium bromide, the solution became blue indicating the loss of cobalt. These observations suggest that the cobalt is in fact chemically bound, but that all of the cobalt may not be completely chelated by the tetradentate amine.

Since both (P-styrene-H)-CH₂-(tet-b) and (P-styrene-H)-CH₂-(tet-b)CoCl₃ are insoluble and do not melt without decomposition, they may not be suitable for casting films either from a melt or from solution. Since a number of proposed studies require the use of films, a new synthetic approach has been employed. A film is cast from a solution containing both (P-styrene-H)-CH₂Cl and tet-b. The film is then heated at 90°C for several hrs. The resulting film is insoluble in all solvents tried thus far but usually swells several fold. A portion of this film was extracted for two hrs with tetrahydrofuran which resulted in a 20% weight loss. Since the original film contained 35% tet-b, at least 15% of the tet-b was not extractable although the (P-styrene-H)-CH₂Cl and tet-b are very soluble in tetrahydrofuran. This observation is consistent with the chemical binding of tet-b to the polymer. The film was metallated with CoCl₂ and analyzed for cobalt. The film was 0.50 \pm .09% cobalt. The large standard derivation results from the low cobalt content and small sample size.

PERSONNEL

Principal Investigator: James L. Reed
Graduate Student: Eric Daley
Postdoctoral: Sivanananda Jada

Subsequent Submissions

Since the preparation of the request for funding by the Office of Naval Research, a research proposal has been submitted to the Department of Energy. Both the concept paper and the proposals have received favorable responses and the full proposal is currently being reviewed. The request to the Department of Energy was for one year at a level of \$60,755.00. The proposed work involved the study of charge transfer states.

Project #6

Synthesis and Characterization of "Comb-Like" Liquid Crystalline
Ion-Containing Polymers

Principal Investigators: Y. H. Mariam
K. B. Bota

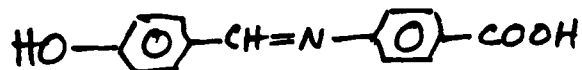
DESCRIPTION OF PROJECT

The purpose of this research project is to synthesize and characterize a new class of ionomers and/or ion-containing polymers whose pendant charged groups contain monomeric liquid crystalline moieties. The inherent liquid-crystalline-phase character and ionic association interactions are expected to reinforce each other leading to enhanced spatial organization of the multiplets and clusters postulated to exist in ionomers. Such a combination should result in improved properties such as high-strength ionomers as well as in possible improvements of liquid crystalline properties (of comb-like liquid crystalline polymers) in the transverse direction. We plan to study the flexibility of the main chain of the polymers, the chemical character of the mesogenic groups and the extent to which the motions of the main chain and the mesogenic group are coupled. The likely possibility that these polymers may be useful for physicochemical model systems that will enhance our understanding of the spatial organization of the multiplets and clusters postulated to exist in ionomers will be evaluated systematically. NMR characterization will be made to elucidate the molecular dynamics and structure of the polymers and to determine the microstructure and microdynamics of the associate counterions. Other characterizations will include differential scanning calorimetry, optical microscopy, viscometry, etc.

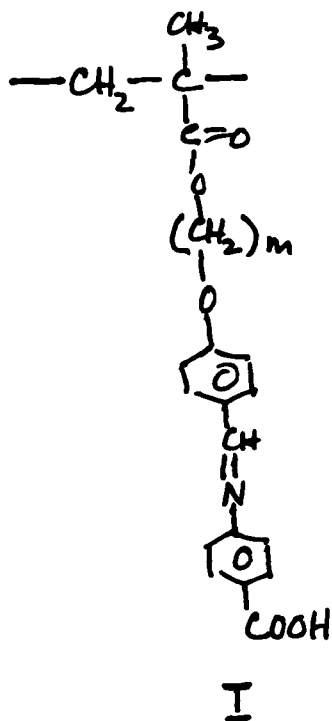
Work Accomplished

I. Update of Last Progress Report

We had indicated in our last progress report that, of the four mesogenic groups synthesized in our laboratory, we had intended to couple the mesogen with the following chemical structure

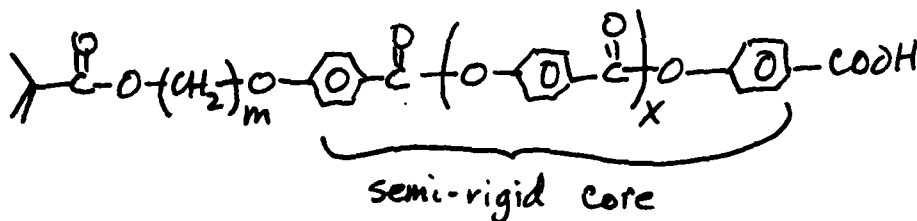


to two spacers for subsequent preparation of the corresponding monomers and finally to prepare two polymers having the following general structure:

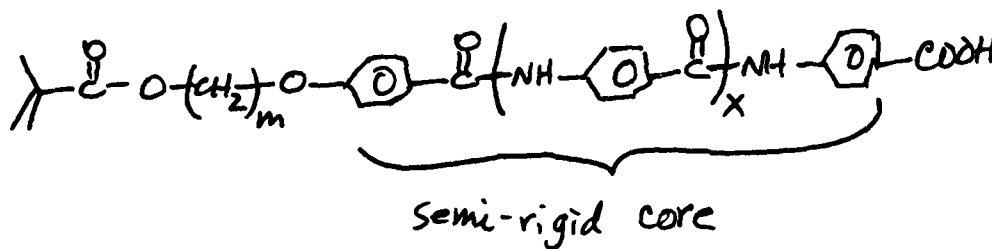


where $m = 0, 2, 3$, etc.

We have accomplished the synthesis of the monomers having $m = 0$ and 3. Our ^1H NMR results on these monomers (will be discussed under experimental part) showed that the mesogenic group, $-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{COOH}$, is not a stable moiety. During the purification (recrystallization) of these monomers, cleavage of the above moiety was observed. Due to this unstable nature of the above mesogenic group it is imperative to modify our purification procedures and we have decided for now to pursue other avenues by incorporating more stable mesogenic groups into polymer structure I. Moieties shown in monomers II and III



II



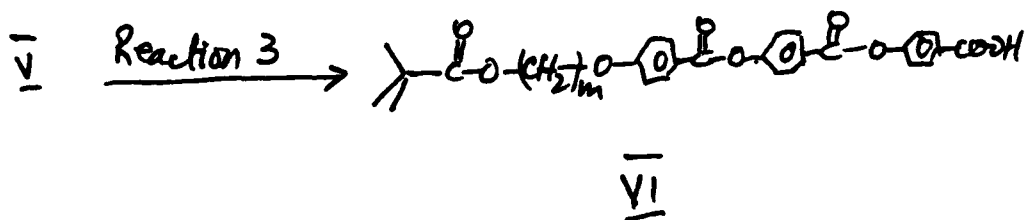
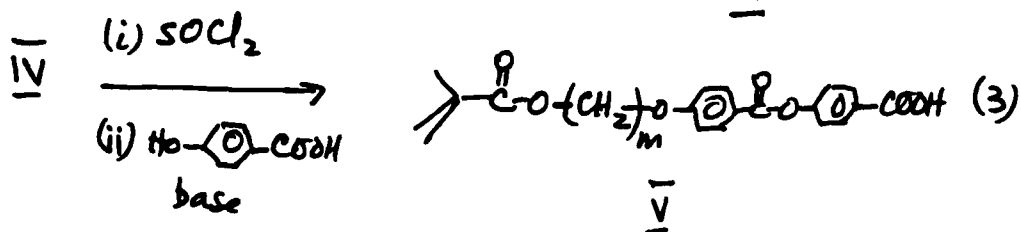
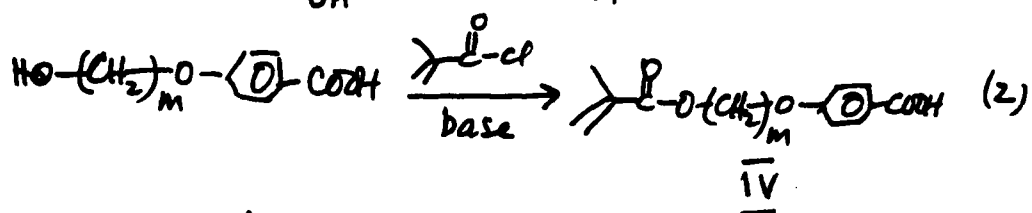
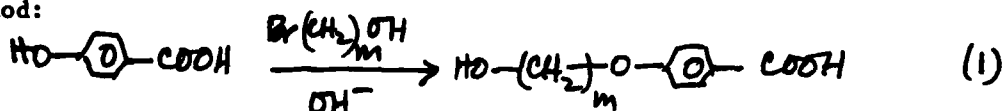
III

where, $x = 0, 1, 2, 3$, etc.

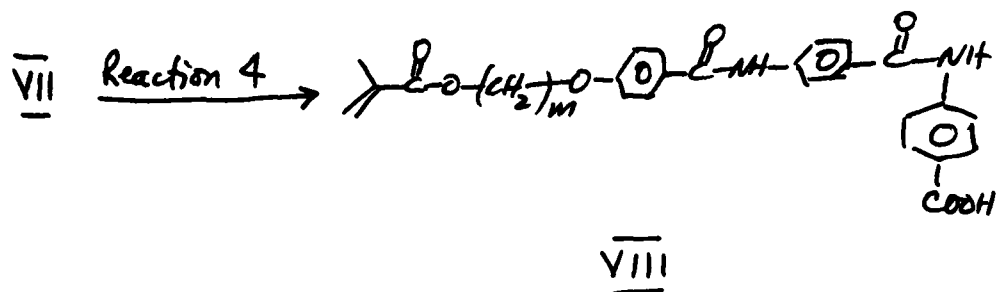
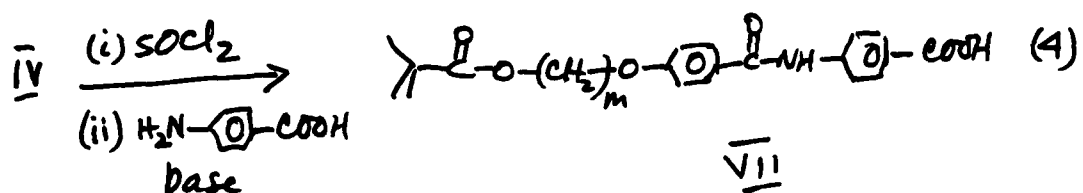
are expected to be much more stable compared to the Schiff base and are selected for this purpose.

The rigid core of the monomer II is a known mesogenic group I. Stiffness of the $-\text{NH}-\text{C}(=\text{O})-$ groups of the monomer III is also expected to impart liquid crystalline properties to monomer III and to its homopolymer.

The above monomers (II and III) could be synthesized by the following method:

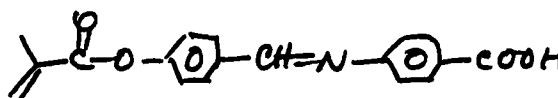


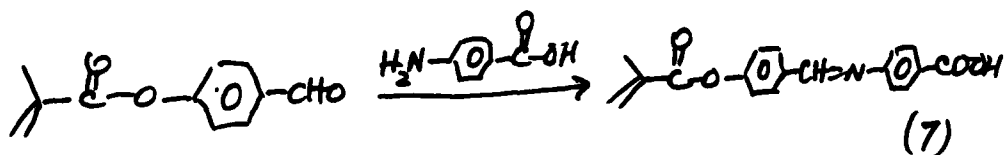
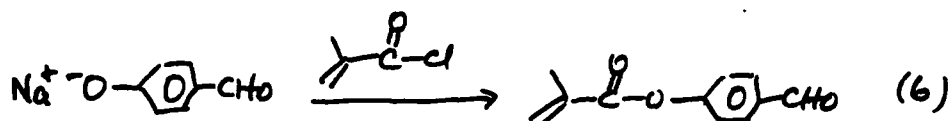
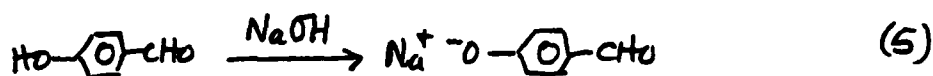
(1) H. Finkelmann and H. J. Wendorff, Polym. Preprints, 24, 24 (2), 1983.



The synthesis of IV having $m = 0, 2, 3$ has already been accomplished. For the comparison purposes, monomer IV (having $m = 3$) has been polymerized. The syntheses of V, VI, VII, and VIII are now in progress.

Work Completed

1. Synthesis of :



A. Reaction (5)

Sodium hydroxide, 4.0g (100 mmoles), was dissolved in 50ml of methanol at room temperature and 10.2g (83.5 mmoles) of p-hydroxy benzaldehyde was added and stirred for 1 hour. The sodium salt was precipitated by adding excess ether to the above solution at room temperature. The precipitate was filtered off and dried. The yield of the crude product was 12.4g.

B. Reaction (6)

The dried crude product of reaction 5 was suspended in CH_2Cl_2 and cooled in an ice bath. Methacryloyl chloride, 7.8g (74.3 mmoles), was added dropwise into the above suspension with vigorous stirring. After a reaction period of 2 hrs, the reaction mixture was extracted with water,

dried over MgSO_4 and the CH_2Cl_2 was evaporated. A yellow colored liquid was obtained. The proton NMR spectrum showed the presence of the following peaks:

- (i) 9.97 (δ) ppm (aldehyde), singlet
- (ii) 7.33 (δ) ppm (aromatic), quartet
- (iii) 5.73 (δ) ppm, (vinyl), singlet
6.35 (δ) ppm, (vinyl), singlet
- (iv) 2.0 (δ) ppm, (methyl), singlet

The integrated area ratio of peak (i) to peak (iv) was 1:3.

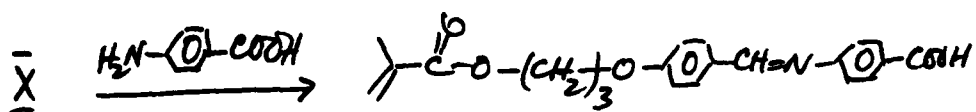
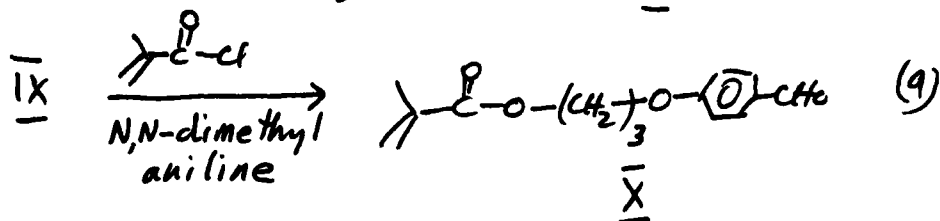
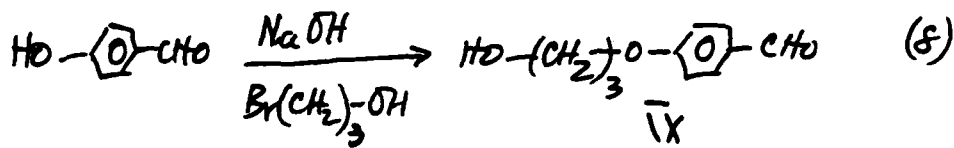
C. Reaction (7)

The crude product of reaction 6, 15.0g (78.0 mmole), was dissolved in 400ml of absolute ethanol and p-aminobenzoic acid, 10.8g (78.9 mmole), was added. The resulting mixture was refluxed overnight and the volume was reduced to 200 mls by distilling off ethanol under reduced pressure. Upon cooling this product, an orange colored product was precipitated out. The crude product was filtered off and dried. The ^1H NMR spectrum showed the presence of the following peaks:

- (i) 8.77 ppm (δ), singlet ($-\text{CH}=\text{N}-$ proton)
- (ii) 7.83 ppm (δ), multiplet (aromatic protons)
- (iii) 6.0 ppm (δ), singlet (vinyl proton)
6.43 ppm (δ), singlet (vinyl proton)
- (iv) 2.06 ppm (δ), singlet (methyl proton)
- (v) 10.16 ppm (δ), singlet (aldehyde protons from unreacted aldehyde).

The integrated area ratio of peak iv to peak v was 18:1, and indicates the presence of free aldehyde. Hence, it was recrystallized from absolute ethanol and the ^1H NMR spectrum was retaken. The integrated area ratio of the same peaks, of the recrystallized product was this time 10:1, which is indicative of the cleavage of the Schiff base during the recrystallization. The formation of a new quartet at 7.1 (δ) ppm also shows the presence of p-aminobenzoic acid produced by the cleavage of the Schiff base.

2. Synthesis of $\text{Ph-CO-O-(CH}_2\text{)}_3\text{-O-Ph-CH=N-Ph-COOH}$:



A. Reaction (8)

Parahydroxybenzaldehyde, 28.0 (0.23 moles), and sodium hydroxide, 10.0g (0.25 moles) were dissolved in a minimum amount of water. To this solution, 3-bromopropanol, 31.9g (0.23 moles), was added and stirred in boiling water bath for 5 hrs. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 , washed several times with water, dried over MgSO_4 , and the CH_2Cl_2 was evaporated. A yellow colored viscous liquid was obtained. The ^1H NMR spectrum of this crude product (IX) showed the presence of the following peaks:

- (i) 9.8 (δ) ppm, singlet (aldehyde proton)
- (ii) 7.4 (δ) ppm, quartet (aromatic protons)
- (iii) 3.83 (δ) ppm, triplet (methylene protons)
- 4.13 (δ) ppm, triplet (methylene protons)
- (iv) 2.0 (δ) ppm, multiplet (methylene protons)

The integrated intensity ratio of peak (ii) : peak (iii) was 1:1.

B. Reaction (9)

The crude product IX, 19.0g (0.10 moles), was dissolved in 50ml of N,N-dimethylaniline. To this solution, methacryloyl chloride, 16.6g (0.16 moles), was added and stirred at room temperature for 24 hours. The reaction mixture was diluted with 100ml of water, acidified with 2N HCl to pH 2 and extracted into ether. The organic layer was washed several times with water, dried over MgSO_4 and the ether was evaporated.

A viscous yellow liquid was obtained. The ^1H NMR spectrum of this crude product (X) showed the presence of the following new peaks (compare with spectrum #4):

- (i) 1.93 (δ) ppm, singlet (methyl protons)
- (ii) 5.6 (δ) ppm, singlet (vinyl proton)
- (iii) 6. (δ) ppm, singlet (vinyl proton)

The integrated intensity ratio of the aldehyde peak (at 9.93 ppm) to the methyl peak was 1:3.

C. Reaction (10)

The crude product, X, 18.0g (72.6 mmole), was dissolved in 400ml of absolute ethanol and p-aminobenzoic acid, 10.0g (72.9 mmole), was added. The reaction mixture was refluxed overnight and the volume was reduced to 200ml by evaporating under reduced pressure. Upon cooling, a yellow colored solid precipitated out. The solid product was filtered off and dried. The ^1H NMR spectrum showed the formation of a new peak at 8.36 ppm (δ) for $-\text{CH}=\text{N}-$ protons (compared to spectrum of X). However, the peak at 10.06 ppm (δ) indicate that the crude product XI contains free aldehyde.

3. Synthesis of :

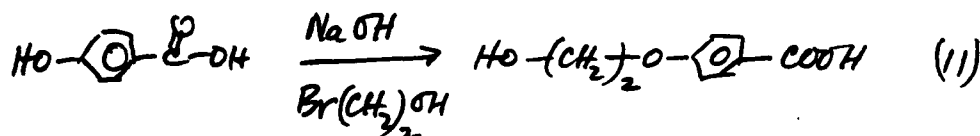
Parahydroxybenzoic acid, 10.0g (72.4 mmole), and sodium hydroxide, 4.9g (0.12 mole), were dissolved in 32ml of water and cooled to 0°C. Methacryloyl chloride, 7.6g (72.4 mmole), was added to the above mixture

and shaken for 25 minutes. The product was acidified with 2N HCl and filtered. A white colored solid product was obtained. This was washed several times with water and recrystallized from a mixture containing methanol and water. The ^1H NMR spectrum of the recrystallized product showed the presence of the following peaks:

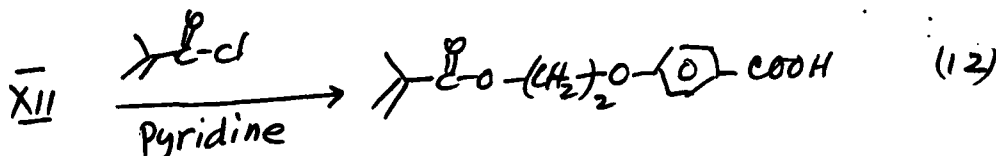
- (i) 7.77 (δ) ppm, quartet (aromatic proton)
- (ii) 6.0 (δ) ppm, singlet (vinyl proton)
- 6.43 (δ) ppm, singlet (vinyl proton)
- (iii) 2.13 (δ) ppm, singlet (methyl proton)

The integrated area ratio of peak (ii) to peak (i) was 1:2.

4. Synthesis of $\text{CH}_3\text{COO}(\text{CH}_2)_2\text{O}-\text{C}_6\text{H}_4-\text{COOH}$:



XII



XIII

A. Reaction (11)

Parahydroxybenzoic acid, 30.0g (0.22 moles), and sodium hydroxide, 17.4g (0.46 mole), were dissolved in a minimum amount of water. To this

solution, 3-bromoethanol, 27.2g (0.22 moles), was added and refluxed on a boiling water for 5 hours. The reaction mixture was cooled to room temperature and acidified with 2N HCl. The solid product obtained was filtered, washed with water and recrystallized from a mixture containing methanol and water. The yield of the recrystallized product was 23.0g. The ^1H NMR spectrum of the recrystallized product (XII) showed the presence of the following peaks.

- (i) 6.55 (δ) ppm, quartet (aromatic protons)
- (ii) 2.93 (δ) ppm, multiplet (methylene protons)

The integrated area ratio of peak (i) to peak (ii) was 1.1:1.

B. Reaction (12)

The recrystallized product XII, 15.0g (82.4 mmole), methacryloyl chloride, 9.0g (85.7 mmole) and 0.5g of hydroquinone was dissolved in a minimum amount of THF at 90°C on a water bath. To this solution, pyridine, 6.6g (83.5 mmole), was added dropwise from a dropping funnel over a four-hour period with vigorous stirring. The THF was evaporated and the residue was acidified with 2N HCl, filtered and washed with water. The crude product obtained was recrystallized from a mixture containing methanol and water.

The ^1H NMR spectrum of the recrystallized product XIII showed the presence of the following peaks:

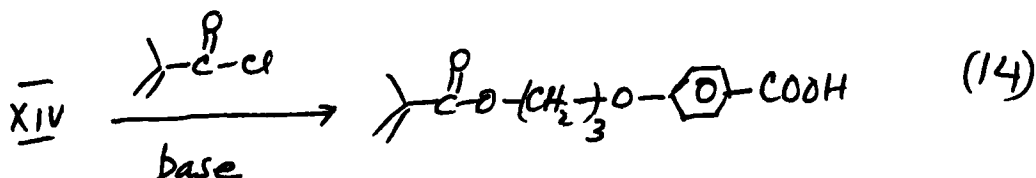
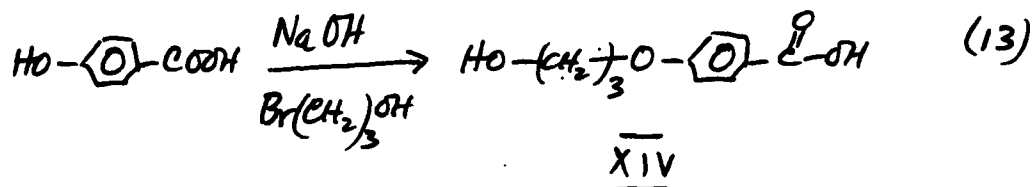
- (i) 7.95 (δ) ppm, quartet (aromatic protons)
- (ii) 5.8 (δ) ppm, singlet (vinyl proton)
- 6.17 (δ) ppm, singlet (vinyl proton)

(iii) 4.5 (δ) ppm, broad singlet (methylene protons)

(iv) 1.95 (δ) ppm, singlet (methyl proton)

The integrated area ratio of peak (iii) to peak (iv) was 4:3.

5. Synthesis of $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4\text{COOH}$:



XV

A. Reaction (13)

Parahydroxybenzoic acid, 40.0g (0.29 moles), and sodium hydroxide, 23.8g (0.6 moles), were dissolved in a minimum amount of water. To this solution, 3-bromopropanol, 40.3g (0.29 moles), was added and refluxed on a boiling water bath for 5 hours. The reaction mixture was cooled to room temperature and acidified with 2N HCl. The solid product obtained was filtered, washed with water and recrystallized from a mixture containing methanol and water.

The recrystallized product, XIV exhibited the following ^1H NMR peaks:

- (i) 7.54 (δ) ppm, quartet (aromatic protons)
- (ii) 3.76 (δ) ppm, singlet (methylene protons)
- (iii) 4.13 (δ) ppm, singlet (methylene protons)
- (iv) 2.0 (δ) ppm, multiplet (methylene protons)

The integrated area ratio of the aromatic peaks to that of the methylene protons was 4:6.

B. Reaction (14)

The recrystallized product XIV, 8.0g (40.8 mmole), methacryloyl chloride, 4.7g (44.8 mmole) and 0.5g of hydroquinone was dissolved in a minimum amount of THF at 90°C on a water bath. To this solution, N, N-dimethyl aniline, 5.0g (41.3 mmole) was added dropwise from a dropping funnel over a period of 4 hours with vigorous stirring. The THF was evaporated and the residue was acidified with 2N HCl, filtered and washed with water. The crude product obtained was recrystallized from a mixture containing methanol and water.

The recrystallized product, XV exhibited the following ^1H NMR peaks.

- (i) 7.55 (δ) ppm, quartet (aromatic protons)
- (ii) 5.70 (δ) ppm, singlet (vinyl proton)
- 6.13 (δ) ppm, singlet (vinyl proton)
- (iii) 4.27 (δ) ppm, multiplet (methylene protons)

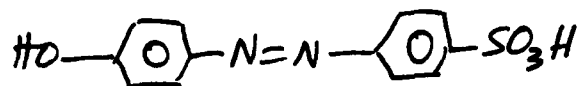
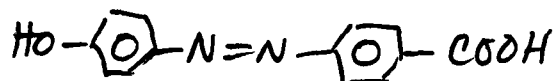
(iv) 2.15 (δ) ppm, multiplet (methylene protons)

(v) 1.93 (δ) ppm, singlet (methylene protons)

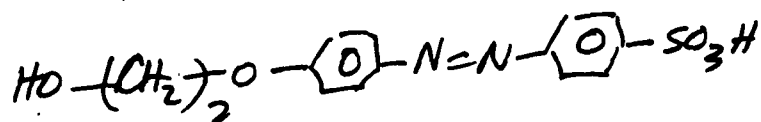
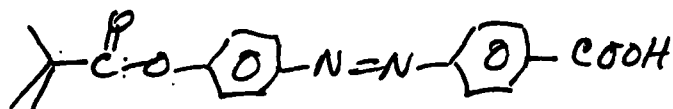
The integrated area ratio of the aromatic peaks to that of the vinyl protons was 4:1.81.

6. Synthesis of Azo Compounds:

The syntheses of the following mesogenic groups

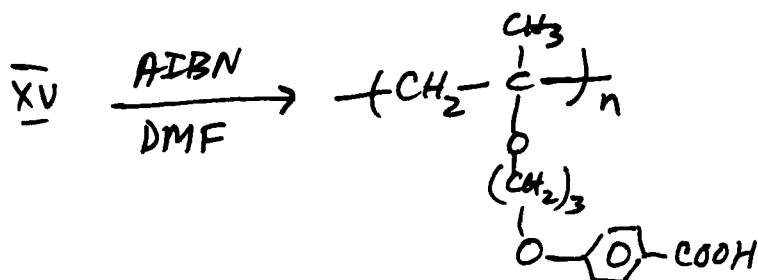
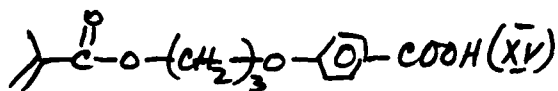


have been completed and NMR data show the expected resonances. Furthermore the syntheses of the following compounds



have been completed. These compounds and others containing the above mesogens that are being synthesized are being and will be characterized by various techniques for proper identification of the compounds.

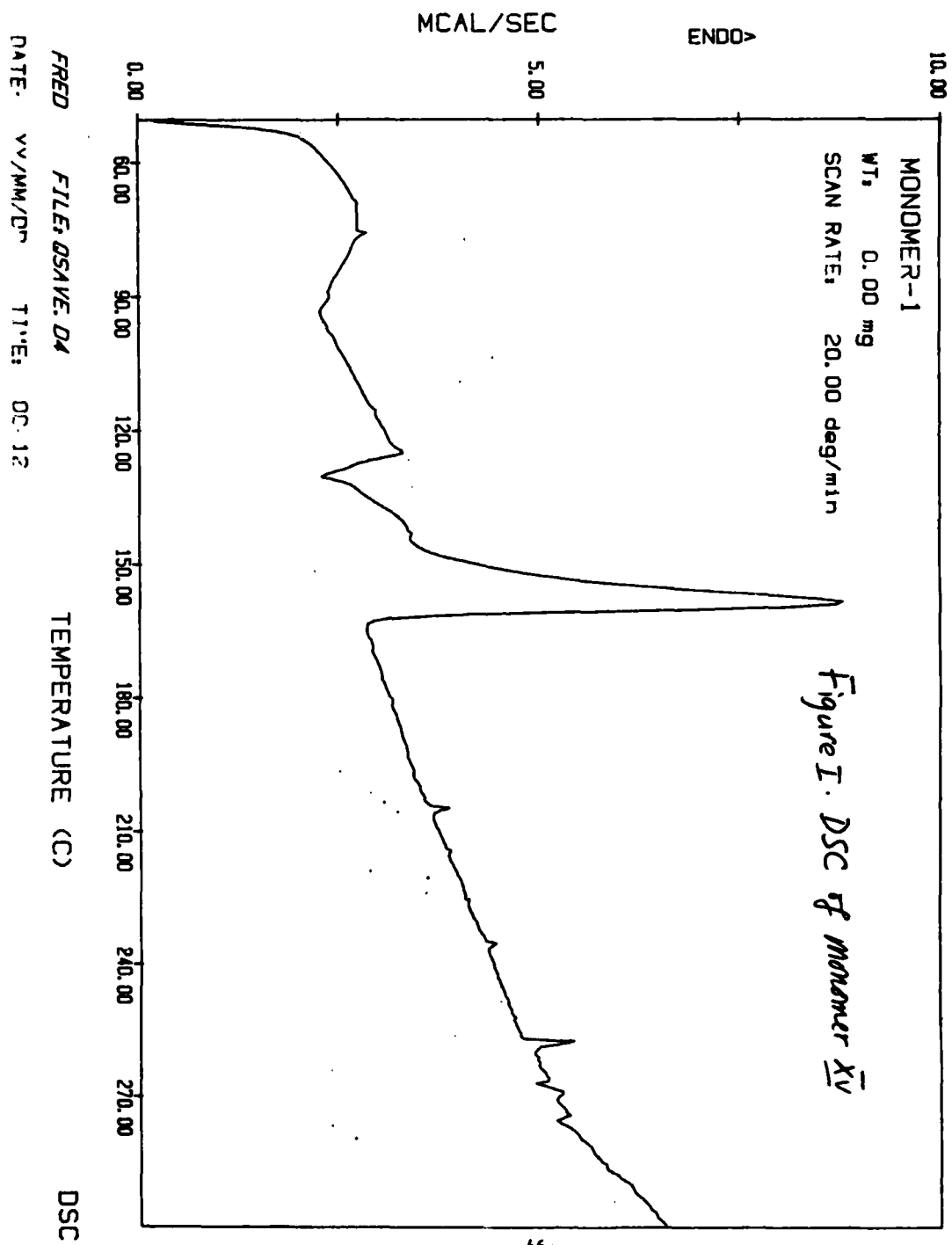
7. Polymerization of

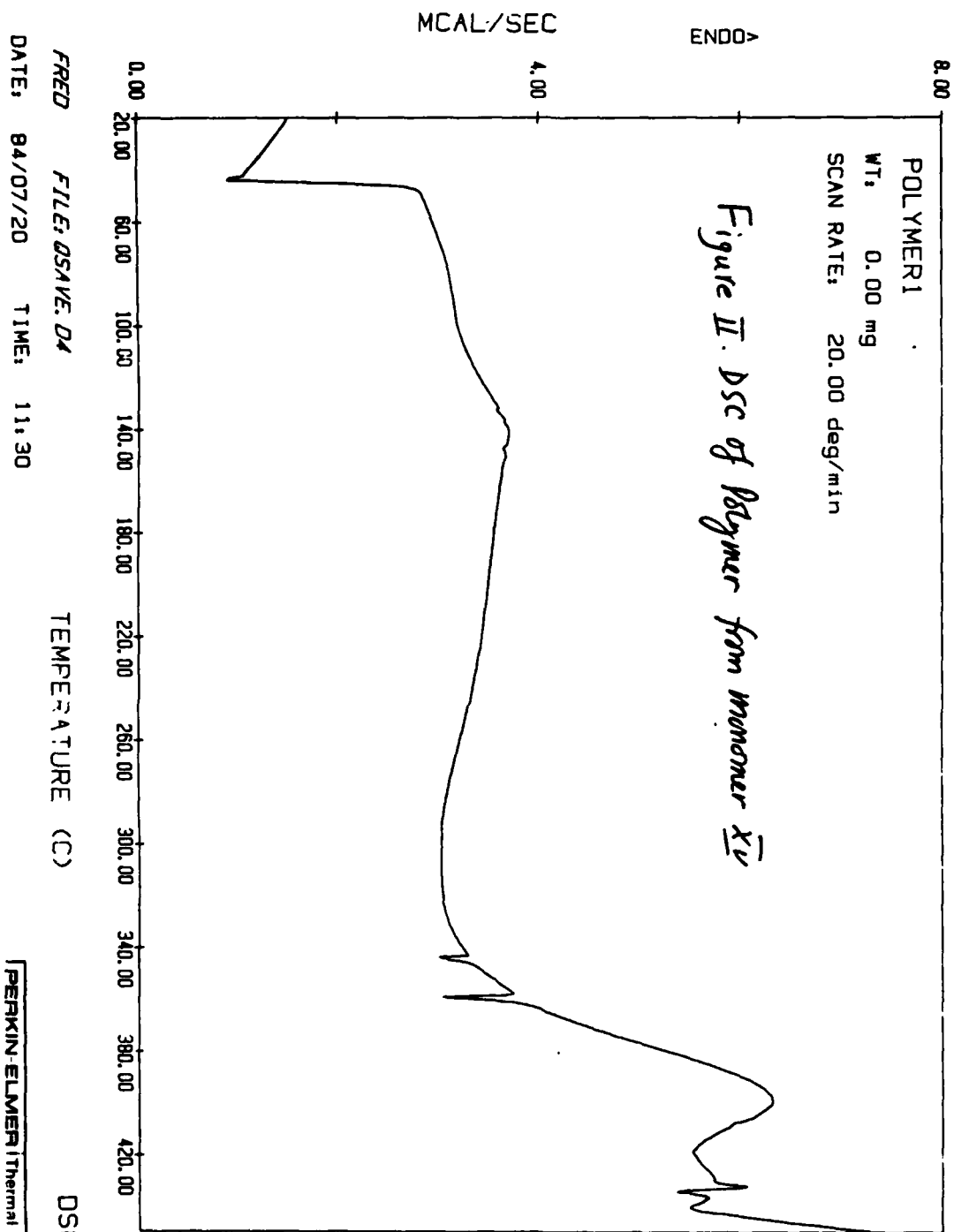


The monomer, XV, 6.0g (24.0 mmole) was dissolved in 10 mls of DMF and degassed with N₂ for 2 hours. To this reaction mixture, 10mg of AIBN was added and heated to 70°C. After a reaction period of 5 hours a gel-like polymer was obtained. It was extracted with 200ml of DMF and finally with water and dried.

III. Results

The DSC curves of the monomer (XV) and its homopolymer are given in Figures I and II. The monomer has a sharp melting point at 158.8°C. The DSC thermogram shows a phase transition at 45°C. The nature of this transition should be confirmed by optical microscopy and other techniques. The polymer of XV has a melting point of 375°C and a small endothermic peak at 432.5°C. This small endothermic peak could be due to clearing of a liquid crystalline phase. Above 450°C, the polymer shows a large exotherm probably due to decomposition. Once again, the characteristics of the transition observed at 432.5°C should be confirmed by other





PERKIN-ELMER Thermal Analysis

techniques. The transition observed at 137°C could be the glass transition of the polymer.

Manpower Training

Four graduate students have been involved in our project. During the initial phase, the emphasis has been to familiarize the students with the literature. Currently all the students are involved in synthesis so that they can be exposed to some synthetic approaches. Later they will be involved in characterization of polymers by different techniques. These students are encouraged to work independently but are also encouraged to interact with K.P. Pemawansa, who is a research associate in our group since the beginning of January.

Mariam and staff (Bota, Collins, Olabisi) are scheduled to teach a new course "Topics in Polymer Chemistry" in the fall of 1984. The course will cover primarily polymer spectroscopy but an overview of topics such as thermal analysis, physical properties of polymers, preceramic polymers, physical chemistry of polymers, etc. will be covered. Mariam plans to eventually teach a polymer spectroscopy course so that other topics can be covered in depth in the "Topics in Polymer Chemistry" course.

Activities to Generate Other Resources

Two proposals have been submitted and at least one other proposal shall be submitted soon.

- A. "Self Reinforcement in Polymer Blends
Principal Investigators: Y. Habte-Mariam, K. B. Bota, and
O. Olabisi

Source: NASA
Requested Amount: \$173,418.00

Period of Support: 9/1/84 - 8/31/87
Percent Effort: 25% (ACAD), 33% (SUMM)

- B. "Acquisition of Accessories for a 200 MHz NMR Spectrometer for Applications to Polymer and Other Material Systems"

Source: NSF
Requested Amount: \$111,400.00
Period of Support: 9/1/84 - 8/31/85

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